DISTRIBUTION OF METAL CONTAMINANTS IN AZARE GROUNDWATER SYSTEM

BY

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DECLARATION

I declare that the work in this thesis entitled **'Distribution of Metal Contaminants in Azare Groundwater System'** has been performed by me in the Department of Chemistry under the supervision of Dr. C.E. Gimba, Prof. A.J. Nok and Dr. L. Salihu.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any university.

Akinola, Lukman Kehinde

| --- | --- | --- |
| Name of student | Signature | Date |

CERTIFICATION

This thesis entitled "DISTRIBUTION OF METAL CONTAMINANTS IN AZARE GROUNDWATER SYSTEM" by Akinola Lukman Kehinde meets the regulations governing the award of Master of Science degree of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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ABSTRACT

The distribution of metal contaminants in Azare groundwater system was investigated in this study. Concentrations of total and soluble forms of K, Ca, Mg, Cu, Zn, Mn, Pb and Cd were determined in randomly selected twenty boreholes and twenty hand-dug wells within Azare town using flame Atomic Absorption Spectroscopy. Findings revealed that, the mean total concentrations of K, Ca, Mg, Cu, Zn, Mn, Pb and Cd in borehole waters were 0.3233±0.2455mg/L, 0.5433±0.1762mg/L, 0.3178±0.1641mg/L, 0.2386± 0.1361mg/L, 0.3260 ± 0.3187mg/L, 0.1879± 0.1082mg/L, 0.1234 ± 0.1480mg/L, and 0.0049 ± 0.0037mg/L respectively while the mean total concentrations of K, Ca, Mg, Cu, Zn, Mn, Pb and Cd in well waters were 0.8790± 90.6823mg/L, 1.1923±1.1337mg/L, 0.9543±1.0186mg/L, 0.0953± 0.1083mg/L, 0.1890±0.0791mg/L, 0.1645±0.1238mg/L, 0.0965± 0.0491mg/L, and 0.0041±0.0034mg/L respectively. It was also discovered that in all the samples investigated, concentrations of Cu and Zn were found below the Maximum Contaminant Levels (MCLs) for these metals in drinking water (MCL for Cu = 1.3mg/L and MCL for Zn = 5.0mg/L) while the total concentration of Pb exceeded the MCL for this metal in drinking water (MCL for Pb = 0.015mg/L). Concentrations of total Mn exceeded the MCL for this metal (0.05mg/L) in all the borehole waters investigated but it only exceeded the MCL for this metal in 95% of the well waters investigated. The concentrations of total Cd was found to exceed the MCL for this metal (0.005mg/L) in 45% of the borehole waters and 35% of the well waters investigated in this study. Apart from K and Cu, no significant differences were found between the mean concentrations of total metal contaminants in boreholes and hand-dug wells investigated. Findings also revealed that on the average, K, Ca, Mg, Zn and Mn exist predominantly in the soluble phase while Cu, Pb and Cd exist predominantly in the particulate phase. The average proportions of the soluble forms of these metals in boreholes were 84.9% for K, 80.5% for Ca, 88.6% for Mg, 22.2% for Cu, 67.2% for Zn, 56.8% for Mn, 39.9% for Pb and 17.5% for Cd while the average proportions of the soluble forms of these metals in hand-dug wells were 93.1% for K, 87.6% for Ca, 91.8% for Mg, 25.5% for Cu, 69.3% for Zn, 76.5% for Mn, 44.5% for Pb and 42.5% for Cd. Implications of the findings were discussed and some useful suggestions given.

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ABBREVIATIONS, DEFINITIONS AND SYMBOLS

AAS Atomic Absorption Spectrometry

MIBK Methyl isobutyl ketone

APDC Ammonium Pyrolidine dithiocarbamate

DDDC Diethylammonium diethyldithiocarbamate

EPA Environmental Protection Agency

USGS United States Geological Survey

WHO World Health Organization

ATSDR Agency for Toxic Substances and Disease Registry

MCL Maximum Contaminant Level

US United States

RNA Ribonucleic Acid

DNA Deoxyribonucleic Acid

ND Not Detected

mg/L Milligram per liter

µg/L Microgram per liter

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the Study

Azare is the headquarter of Katagum local government area in Bauchi state of Nigeria. It has a population of over one hundred and fifty thousands according to the 1991 population census (Shehu, 2000). Azare is often regarded as the second most developed city in the state, in terms of provision of social amenities. However, majority of the people in Azare, according to Alabi (2005), still depend on groundwater (bore-holes and wells) for drinking and other domestic purposes. It is an age-long belief among the people that groundwater is pure and safe for drinking but recent discoveries have shown that like surface water, groundwater is also vulnerable to contamination from a variety of sources (Texas Environmental Profiles, 2003). According to Ademoroti (1996), groundwater contamination may be from seepages from agricultural activities, septic systems, and mining activities and even from geological origin.

Assessing the dangers from metallic contaminants to human healths involves concerns that are different from those associated with organic chemicals. Organic chemicals are generally broken down over time in the

environment but metals are not and can easily be accumulated and concentrated in living systems (Chemical and Engineering News, 2002).

The considerable interest in, and apprehension about the role and fate of metals in aquatic systems, as displayed by scientists and regulatory bodies, is warranted on the grounds of several disasters which are related to mercury and cadmium poisoning (Forstner and Wittmann, 1979). Although, metals such as sodium, potassium, magnesium, calcium, manganese, iron, cobalt, copper and zinc have been shown to be essential to human life (Shriver and Atkins, 1999) but studies pertaining to the toxicity of these trace metals, according to Forstner and Wittmann (1979), follow the general trend that an undersupply leads to deficiency symptoms, sufficient supply results in optimum conditions, and an oversupply results in toxic effects and lethality in the end.

Until recently, most environmental research on trace metals were based on the assessment of the total metal concentration but it is becoming increasingly evident that the impact of a particular metal species may be more important than the total metal concentration (Johansson, 1996). It has also been observed by Goulden (1978) that the toxic effect of metals such as lead, cadmium and mercury depends largely on whether the metals exist in a form that is physically available to the living organism rather than the total

concentration of the toxic metals. Forstner and Wittmann (1979) reported that when large quantities of silver in the form of soluble silver ions are ingested, they remain impregnated in tissues forming a stable bond to —SH or —SR groupings and this has been shown to be responsible for the permanent discolouration of skin and eye tissue, a condition known as argyria. However, most insoluble salts do not pose any health risk to human if ingested because they are merely excreted in faeces.

A study carried out by Saje (2005) on the determination of heavy metal constituents of groundwater samples in Azare is considered to be the only work on Azare groundwater system. The work is inadequate on two grounds. First, the study is limited in scope both in terms of the number of samples analyzed and the number of heavy metals determined (only three metals – Cu, Pb and Zn – were determined in three bore-holes and three wells). Second, the study was also restricted to the determination of total heavy metal concentrations in the groundwater samples. On the basis of these limitations, findings from the study lack the validity for generalization. The present study focuses on the determination of metal contaminants in Azare groundwater system on a broader scope with a view to understanding the distribution patterns of the metals in groundwater system.

1.2 Purpose of the Study

The general purpose of this study is to investigate the pattern of distribution of metal contaminants in Azare groundwater system. Specifically, the study aims at achieving the following objectives:

(i) To compare the total concentrations of the metal contaminants in Azare groundwater system with the maximum contaminant level for drinking water standards.

(ii) To compare the total concentrations of the metal contaminants in bore-holes with those in wells.

(iii) To determine the distribution of each metal contaminant between the dissolved phase and the suspended sediment in groundwater.

1.3 Research Hypothesis

In order to achieve the second objective stated under section 1.2 above, the following null hypothesis was formulated and tested at 0.01 level of significance.

Ho: There is no significant difference between the mean total concentrations of metals in bore-holes and their respective mean total concentrations in hand-dug wells.

1.4 Significance of the Study

It is expected that the findings from this study will be of great importance to researchers in the field of environmental chemistry and the community in which the samples for the study were collected. Investigators in environmental chemistry will benefit in three ways. First, the study will provide a base line data so that, the impact of man's activities on the quality of groundwater in Azare, as far as trace metals are concerned, can be assessed in the future. Second, the study will enable researchers to know if bore-holes are more vulnerable to contamination by metals than hand-dug wells or vice-versa. Third, findings from this study will provide an insight into the natural distribution of metals between the dissolved and the particulate phases in groundwater.

The People of Azare will also benefit from this study because the findings thereof will enable them to know the extent at which the ground waters in Azare have been contaminated by metals.

1.5 Scope and Limitation of the Study

This study is a preliminary investigation geared towards understanding the distribution of metal contaminants in Azare groundwater system. Detailed determination of the various forms in which each metal

contaminant exists in both the dissolved and the particulate phases will not be investigated. This limitation is imposed on this study because of the lack of necessary facilities needed to accomplish this aspect of the research.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1. Hydrological Cycle and Self-purification Mechanism of Water

Since very ancient times, it has been empirically known that there is a hydrological cycle (or water cycle). Nace (1976) noted that water circulates naturally through five principal realms. These realms are; oceans, atmosphere, lakes and rivers; icecaps and glaciers; and underground water. Air and water are the most mobile physical components of the earth system, and this mobility permits the hydrological cycle to operate. Constant circulation of water from ocean to atmosphere occurs through evaporation, and from the atmosphere to land areas or directly back to the ocean through condensation (Nace, 1976). It has also been shown that water also circulates from land and vegetation to the atmosphere through evaporation and transpiration respectively (Down and Stocks, 1977). Through runoff and percolation, water from the land, according to Down and Stocks (1977), can also get into the ocean, lakes, rivers and streams.

It has been observed that groundwater is a long-term reservoir of the natural water cycle, as opposed to short-term water reservoir like the atmosphere and fresh surface water (Fabrizi, 2005). Ground waters are linked to rivers and lakes in a more direct physical way. As pointed out by

Williams *et al* (1993), where the amount of water lost due to evaporation is greater than the amount gained due to precipitation, consequently rivers and lakes are often fed by slow seepage from the groundwater stored in higher parts of the landscape. Such seepage according to Willams *et al* (1993) helps to sustain river flow during dry season and similarly helps to maintain lake levels during the same period. In arid regions however, the reverse may be the case; river flow is lost through the porous stream-bed into the underlying alluvium, where it recharges to groundwater store.

The hydrological cycle, according to Down and Stock (1977), contains within it, two self-purifying mechanisms. The first of these mechanisms is that due to evaporation from the earth's surface together with transpiration from vegetation. These two processes are collectively termed evapotranspiration. Evapotranspiration ensures that the water vapour returned to the atmosphere is purified. The second mechanism is filtration, which occurs when water falling on the land surface percolates into the substrata and permeates through them. It should however be noted that, there are some pollutant molecules which are either too volatile or too small to bypass the two major purification mechanisms discussed above.

The phenomenon of hydrological cycle is very important if one considers the transportation of wastes via air, water and land. Contamination

in one part of the earth could result in contamination in another part of the earth.

2.2. Sources and Effects of Metal Contaminants in Groundwater System

The overwhelming majority of the earth's water exists in the forms which render it almost unusable directly for man's needs either because of salinity or its physical nature (for instance, ice) or location in the ground (Down and Stocks, 1977). A breakdown of water distribution shows that usable fresh water upon which we mostly rely, comprises no more than 0.0161% of the earth's total water (The New Encyclopedia Britannica, 1975). Surface waters are visible and because tremendous amounts of money are being spent in building dams, artificial reservoirs and irrigation canals, it is a natural tendency to think of surface water as the major source for the world's needs. However, available facts reveal that, of the usable fresh water upon which we mostly rely, less than 3% occurs in the form of surface water while the remaining over 97% is underground water (Briggs, 1976).

Groundwaters, according to Ademoroti (1996), are normally effectively purified as far as suspended matter is concerned by the straining action of the soil as water percolates through it. However, soluble impurities are not so readily removed in the same manner, even though there is the

possibility of ion-exchange reaction in them. Ali et.al (2005) observe that contamination of the aquatic environment in Nigeria is increasing in scope and magnitude due to rapid urbanization and industrialization. The realization of this fact has led to an increasing number of published works on the levels of metal contaminants in both surface water and groundwater in Nigeria (Yahaya and Suleiman, 1999; Isihei and Okiemen, 2000; Edet et.al, 2003; Dike et.al, 2004; and Alagbe, 2006).

Studies have shown that groundwater may be contaminated by both natural and man-made sources. As pointed out by U.S. Geological Survey, USGS (2005), naturally occurring contaminants are present in the rocks and sediments. As groundwater flows through rocks and sediments, metals such as iron and manganese are dissolved and may later be found in high concentrations in the groundwater system. It should be noted that contamination of air, surface water and soil by human being can result in contamination of groundwater system since these contaminants can be transported from any of these regions of the earth to the groundwater system. For instance, Polanska et.al (1993) observed that pollution of groundwater could be caused by infiltration of chemical compounds eluted from stored industrial wastes by rain water.

Five different sources from which metal pollution of the environment originate have been identified by Forstner and Wittmann (1979). These include: geological weathering, industrial processing of ores and metals, the use of metals and metal components, leaching of metals from garbage and solid waste dumps, and animal and human excretions which contain heavy metals. Iwegbue et.al (2006) have suggested that the elevated levels of heavy metals in soil profiles of automobile mechanic waste dumps in Nigeria constitute a serious threat to both surface waters and ground waters. Studies have also shown that anthropogenic contamination of natural water by metals occur through mining activities (Stamatis et.al, 2001; and Lee *et al*., 2005), domestic sewage (Tijani and Onodera, 2005), agricultural and urban wastewaters (Mahiknecht et.al, 2004), and discharge from industrial effluents (Biney *et al.*, 1991). Detailed discussions of the sources and effects of each metal contaminant considered in this study are the focus of the following sub-sections:

2.2.1. **Sources and Effects of Potassium**

Potassium has an atomic number of 19 and it has three naturally occurring isotopes with the following relative abundances; 93.08% for ^{39}k, 0.0119% for ^{40}k, and 6.91% for ^{41}k (Hoefs, 1973). Of the three naturally occurring isotopes of potassium, ^{40}k has been found to be unstable and it

decays by electron capture to yield ^{40}Ar or by beta emission to yield ^{40}Ca (Cocco *et al*, 1970). The potassium content of groundwater is a function of weathering rate of potassium minerals such as potassium – feldspar. The potassium content of groundwater is also affected by the rate of stable potassium mineral formation such as illite, the availability of exchange sites on clay minerals, and of the supply from interstitial solutions (Cocco *et al*, 1970).

Potassium is needed for growth, building muscles, transmission of nerve impulses, and heart activity (Zest for life, 2006a). Potassium together with Sodium (Potassium inside the cell and sodium in the fluid surrounding the cell), work together for the nervous system to transmit messages as well as regulating the contraction of muscles. A deficiency of potassium, according to Zest for Life (2006a), may result in fatigue, cramping legs, muscle weakness, slow reflexes, acne, dry skin, mood changes, and irregular heartbeat.

Although, the concentration of potassium normally found in drinking water has no physical or aesthetic effects on drinking water users, excessive potassium intake can be toxic and will affect the heart of people suffering from problems such as kidney failure (Zest for Life, 2006a). It has been

observed that in normal healthy human being, up to 80 percent and 15 percent of the daily intake of potassium is excreted in urine and faeces respectively while substantial amount is also lost through sweating (Nduka, 1999).

2.2.2. Sources and Effects of Calcium

Calcium has an atomic number of 20 and it has six stable isotopes in the mass-range of 40 to 48. The relative abundances of these stable isotopes of calcium are; 98.88% for ^{40}Ca, 0.0046% for ^{46}Ca, 0.138% for ^{43}Ca, 2.12% for ^{44}Ca, 0.0046% for ^{46}Ca, and 0.20% for ^{48}Ca (Hoefs, 1973).

Calcium is needed for the formation and maintenance of bones, the development of teeth and healthy gums. It is necessary for blood clotting, stabilizes many body functions and it is also thought to assist in bowel cancer. Calcium has a natural calming and tranquilizing effect and it is necessary for maintaining a regular heartbeat and the transmission of nerve impulses. Calcium also helps in lowering cholesterol, muscular growth, prevention of muscle cramps and normal blood clotting (Zest for Life, 2006b). Calcium also helps with protein structuring in DNA and RNA. It provides energy, breaks down fats, maintains proper cell membrane permeability, aids in neuromuscular activity and helps to keep the skin

healthy. Calcium also stops lead from being absorbed into bones (Zest for Life, 2006b).

Prolonged bone re-absorption from chronic dietary deficiency results in osteoporosis, which may result from either too little bone mass accumulation during growth or higher rate of bone loss at menopause. Dietary calcium deficiency has also been associated with increased risk of hypertension and colon cancer. (Zest for Life, 2006b).

Excess calcium supplementation has been associated with some mineral imbalances such as Zinc. Combined with a magnesium deficiency, excess calcium intake may cause deposits to form in human kidneys, which could cause kidney stones. (Zest for Life, 2006b).

2.2.3. Sources and Effects of Magnesium

Magnesium has an atomic number of 12 and it has three stable isotopes with mass numbers 24, 25 and 26 (Usdowski and Meuller, 1970). The relative abundances of these three isotopes of magnesium according to Hoefs (1973) are: 78.8% for ^{24}Mg, 10.15% for ^{25}Mg, and 11.06% for ^{26}Mg.

Magnesium plays an important role in at least 300 fundamental enzymatic reactions in the body and for that reason it is of vital importance

in our health (Prasad, 1978). Magnesium helps in the formation of bone and teeth and assists the absorption of calcium and potassium. While calcium stimulates the muscles, magnesium is used to relax the muscles. Magnesium is further needed for cellular metabolism and the production of energy through its help with enzyme activity. It is used for muscles tone of the heart and assists in controlling blood pressure. Magnesium can help in preventing the calcification of soft tissue and may help prevent cardiovascular disease, Osteoporosis, and certain forms of cancer. It may also reduce the cholesterol levels in the body. Magnesium also assists the parathyroid gland to process Vitamin D (Zest for Life, 2006c).

There are many causes of clinical magnesium deficiency. These, according to Prasad (1978), include gastrointestinal and nutritional causes, renal causes, endocrine and metabolic causes. Many cardiovascular problems are indicated with magnesium deficiency. Rapid heart beats as well as fatigue, irritability, and seizure can occur. Insomnia, poor memory, painful periods, depression, hypertension and confusion may also be indicative of magnesium in short supply (Zest for Life, 2006c).

Intoxication and hypermagnesemia occur mainly in patients with serious renal insufficiency and in eclampsia when large doses of magnesium

salts are administered. It appears that excess magnesium blocks neuromuscular transmission owing to diminution in endo-plate potential. Infants born to mothers receiving $MgSO_4$ treatment for eclampsia are at risk of developing intoxication manifested as depression and hypotonia (Prasad, 1978).

2.2.4. Sources and Effects of Copper

Copper has an atomic number of 29. Natural copper consists of two stable isotopes which are ^{63}Cu and ^{65}Cu. Their relative abundances are 68.94% for ^{63}Cu and 31.06% for ^{65}Cu (Zemann and Wedepohl, 1970). Copper is a metal that occurs naturally through the environment. It can be found in rocks, soil, water and air (ATSDR, 2004). According to USGS (2005), copper enters the environment from metal plating, industrial and domestic waste, mining, and mineral leaching. It has also been reported that copper can get into the environment through corrosion of household plumbing systems and erosion of natural deposits (EPA, 2006b). ATSDR (2004) also reported that lakes and rivers that have been treated with copper compounds to control algae, or that receive cooling water from power plants, can have high levels of copper. It has been demonstrated that contamination

of the environment by copper occurs when runoff of precipitation falls on external architecture such as roofing (Ray, 2005).

It has been reported that copper is required in the formation of hemoglobin, red blood cells and bones (Zest for Life, 2006 d). Copper is also necessary for the manufacture of the neurotransmitter, noradrenalin as well as for the pigmentation of human hair. Copper can be stored in human body, and if it is found deficient in the body, iron is also normally in short supply, leading to anemia as well as the likelihood for infections, osteoporosis, thinning of bones, thyroid gland dysfunction, heart disease as well as nervous system problems (Zest for Life, 2006 d). Deficiency of copper in the body was reported by Prasad (1978) to result in failure of pigmentation of hair and wool in numerous mammalian species, spontaneous fractures of bones in sheep and cattle grazing in copper-deficient pastures, impairment of iron in copper-deficient pig, and nervous disorders in the neonates of various species, including lambs, goats, pigs, guinea pigs, and rats.

Although, a small amount of copper is essential for good health (Shriver and Atkins, 1999), oversupply of copper has been shown to constitute health hazard in human beings (Forstner and Wittmann, 1979).

For instance, EPA (2006 b) observed that short term exposure to copper can cause gastrointestinal distress while long term exposure may result in liver or kidney damage. According to ATSDR (2004), ingesting high levels of copper can cause nausea, vomiting, and diarrhea. It has also been reported that presence of copper in natural water can impact an adverse taste on the water and it also brings about significant staining to clothes and fixtures (USGS, 2005).

2.2.5. Sources and Effects of Zinc

Zinc is one of the most ubiquitous trace elements in nature. It has an atomic number of 30 and five stable isotopes with the following relative abundances; 48.89% for ^{64}Zn, 21.81% for ^{66}Zn, 4.11% for ^{67}Zn, 18.56% for ^{68}Zn, and 0.62% for ^{70}Zn (Brehler and Wedepohl, 1970). Although, zinc can be found naturally in water, it usually enters into the environment from industrial waste, metal plating and plumbing (USGS, 2005). It has also been observed that Zinc can contaminate drinking water when such water is stored in metal containers or flows through pipes that have been coated with zinc to resist rust (ATSDR, 2005a).

Zinc is one of the essential elements which is required by human being in trace amount. Some 24 metalloenzymes have been described in

which Zinc is bound in a fixed stochiometric amount to the apoenzyme (Van Rij and Pories, 1980). Zinc is also more loosely associated with other proteins to form metal-enzyme complexes that significantly influence the behaviour of the enzyme. Florence (1980) also noted that Zinc is a component of many enzymes and it is involved in the synthesis of RNA and DNA. It has been reported that Zinc aids in the healing of wounds (USGS, 2005) and it also acts to diminish the toxicity of cadmium and copper (Florence, 1980).

A deficiency of Zinc in the body will result in an under-performance of the immune system, exposure to infection, allergies, night blindness, loss of smell, falling hair, white spots under finger nails, skin problems, and sleep disturbances (Zest for Life, 2006 e). It has also been observed that men with Zinc shortage may have a problem with fertility, while women may experience irregular periods. Children with too little Zinc may have stunted growth and slow sexual maturity (Zest for Life, 2006 e).

Although, trace amount of Zinc is needed by human being, too much of Zinc has been demonstrated to exhibit harmful effects in human being. For instance, ATSDR (2005) noted that harmful effects of Zinc generally begin at levels 10 – 15 times higher than the amount needed for good health.

Large oral doses of zinc even for a short time can cause stomach cramps, nausea, and vomiting. If large doses of zinc are taken for a longer time, it can cause anaemia and decrease the levels of cholesterol in the body (ATSDR, 2005). Although, the effect of taking high levels of zinc on reproduction in human is not known at present, studies on rats showed that rats that were fed with large amounts of zinc became infertile (ATSDR, 2005).

2.2.6. Sources and Effects of Manganese

Manganese has an atomic number of 25. It enables the body to utilize vitamin C, B1, biotin as well as choline. Manganese is also used in the manufacture of fat, sex hormones and breast milk in females. It has been suggested that manganese also helps in neutralizing free radicals and it is also needed for normal nerve function (Zest for Life, 2006f). Deficiency of manganese is rare but if it occurs, it would be manifested as poor bone growth, problems with the disks between the vertebrae, birth defects, and problems with blood glucose levels and reduced fertility. Serious deficiency in children can result in paralysis, deafness and blindness (Zest for Life, 2006 f). It has been noted that deficiencies vary according to animal species and the degree of deficiency. However, many symptoms that are

common to several species of animals include skeletal abnormalities and postural defects. Some other defects in carbohydrate metabolism have also been observed with manganese deficiency (Prasad, 1978).

Toxicity of manganese through diets or drinking water is rare (Zest for Life, 2006 f). However, chronic manganese poisonings have been reported among miners working with manganese ores. The manganese enters the lungs as oxide dust from the air and also enters the body via the gastrointestinal tract. The disease is characterized by a severe psychiatric disorder resembling Schizophrenia, followed by a permanently crippling neurological disorder clinically similar to Parkinson's disease (Prasad, 1978).

2.2.7. Sources and Effects of Lead

Lead has an atomic number of 82. It has four stable isotopes. These are ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb with relative abundances 1.28%, 26.73%, 20.51% and 51.48% respectively (Sahl et.al, 1970). The isotopic abundances of the lead isotopes vary considerably from one lead-ore deposit to the other. This is because three of the isotopes of lead are generated by radioactive decay processes. ^{206}Pb is produced by the decay of ^{238}U, ^{207}Pb by decay of ^{235}U, and ^{208}Pb by decay of ^{232}Th. ^{204}Pb has no long-lived radioactive parent

(Sahl *et al*, 1970). Therefore, the relative abundances shown above for the four isotopes of lead are only the approximate average compositions of the two isotopically extreme for two major lead-producing deposits in the U.S.A.

It has been estimated that approximately 20 percent of human exposure to lead is attributable to lead in drinking water (EPA, 2006 a). One of the major sources of lead in drinking water is water pipes that contain lead solder (ATSDR, 2005). Environmental pollution from lead is mainly a problem arising from the use of tetra alkyl lead compounds as anti-knock additives in petrol. Evaporation losses incurred during transport and handling of leaded petrol and emissions in motor vehicle exhaust are the major sources of lead in the environment. It has been suggested that up to about 3 percent of the tetra alkyl lead in petrol is emitted, either without degradation or as ionic alkyl lead. The bulk of the tetra alkyl lead species is, however, completely combusted and primarily emitted as particulate inorganic lead (Johansson, 1996).

Although the use of tetra alkyl lead is diminishing, the more stable forms, trialkyl lead and dialkyl lead, have been shown to be fairly persistent in the environment (Johansson, 1996). When lead is released into the

atmosphere, it may travel long distances before setting to the ground (ATSDR, 2005). Studies have also shown that, even in remote areas with no direct sources of emission from traffic, the concentrations of alkyl lead species found are related to, and correlated with the introduction and proliferation of motor vehicles (Johansson, 1996). According to Texas Environmental profile (2003), lead and other contaminants could find their ways into groundwater system via abandoned hazardous wastes sites. Other sources of lead in groundwater system, according to USGS (2005), include industry, mining, plumbing, gasoline, and coal and water additives.

The effects of lead are the same whether it enters the body through inhalation or orally. As pointed out by ATSDR (2005), lead can affect almost every organ and system, both in adults and children. According to USGS (2005), lead affects red blood cell chemistry, delays normal physical and mental development in babies and young children. It also causes slight deficits in attention span, hearing, and learning in children. Lead has also been shown to cause a slight increase in blood pressure in some adults. It has also been recorded that long-term exposure of adults to lead can result in decreased performance in some tests that measure functions of the nervous system (ATSDR, 2005).

It has been observed that lead may also cause weakness in fingers, wrists, or ankles and exposure to high lead levels can severely damage the brain and kidneys in adults or children and can ultimately result into death. In pregnant women, high levels of exposure to lead may cause miscarriage and high-level exposure in men can damage the organs responsible for sperm production (ATSDR, 2005).

The biochemical effects of lead in human body have been investigated in detail and findings from such investigations as presented by Prasad (1978) are as follows: Lead inhibits nearly all the enzymatic steps involved in heme synthesis. One of the primary effects of lead is on immature erythrocytes, the production of which appears to be increased by lead. Lead also inhibits the uptake of iron from transferring by the reticulocyte. There is also evidence that globin synthesis is inhibited in the presence of lead, but the mechanism is not known. Lead also affects other heme enzymes, notably cytochrome P_{450} in the liver. An adverse effect of lead on adnyl cylase in brain and pancreas has been observed. A relatively low concentration of lead has been demonstrated to affect collagen synthesis adversely. Lead inhibits lipoamide dehydrogenase, an enzyme crucial to cellular oxidation.

2.2.8. **Sources and Effects of Cadmium**

Cadmium has an atomic number of 48, with eight stable isotopes. The mass numbers of these isotopes are between 106 and 116. The relative abundance of the isotopes are 1.22%, 0.88%, 12.39%, 12.75%, 24.07%, 12.28%, 28.86%, and 7.58% (Wakita and Schmitt,1970). Although, Cadmium is found in low concentrations in rocks, coal, and petroleum and may enter both surface water and groundwater when dissolved by acidic water, most of the cadmium in the environment enter the environment from industrial discharge, mining waste, metal plating, water pipes, batteries, paints and pigments, plastics, stabilizers and landfill leachate (USGS, 2005). According to EPA (2006b), cadmium also enters into drinking water through corrosion of galvanized pipes, erosion of natural deposits, discharge from refineries, and runoff from waste batteries and paints.

It has been shown that cadmium replaces zinc biochemically in the body and causes high blood pressure, liver and kidney damage (USGS, 2005). Cadmium also causes anaemia, destroys testicular tissue and red blood cells, and it is also toxic to aquatic biota (USGS, 2005). According to ATSDR (1999), drinking water with very high levels of cadmium severely irritates the stomach, leading to vomiting and diarrhea. It has also been

reported that animals given cadmium in food or water had high blood pressure, iron-poor blood, liver disease, and nerve or brain damage (ATSDR, 1999). Cadmium stays in the body for a very long time and can build up from many years of exposure to low levels of cadmium.

Although, severe cases of cadmium poisoning are very rare, occasional serious damage to human health has been recorded. The best-known example is that of cadmium-polluted water from a lead-zinc-cadmium mine in Japan where contaminated irrigation water was used in rice paddy fields and since 1946, there have been numerous cases of 'itai–itai' disease, a cadmium-induced degeneration of bones which can proceed to the extent that even coughing can cause multiple fractures of ribs. Up to 1965, nearly 100 deaths from itai–itai disease had been recorded (Down and Stocks, 1977).

2.3. Metal Contaminants and their Maximum Contaminant Levels in Drinking Water.

The importance of determining the adverse effects of chemicals upon human health has gained momentum during the past decade, both on scientific and emotional grounds. The primary reason for setting standards for drinking water, according to Forstner and Wittman (1979), is to protect

human health. Standards for drinking water are intended to limit the concentration of chemicals below levels that produce harmful effects. Although, it is still a difficult task for the scientists to determine the exact effects of potentially harmful chemicals on humans since for ethical reasons, human beings cannot be deliberately exposed to these chemicals, catastrophic episodes of metal poisonings such as the mercury poisoning in Minamata bay, cadmium poisoning in Japan, lead poisoning in Germany, Copper poisoning in Holland, and Chromium poisoning in Tokyo have led to increased awareness of the general public about the potential health hazard of metals in drinking water (Goulden, 1978 and Forstner and Wittman, 1979). In order to safeguard the health of the people, several regulatory bodies such as World Health Organization and United States Environmental Protection Agency have set up drinking water standards in which a list of contaminants and their maximum permissible concentrations in drinking water was prepared.

There are two types of drinking water standards according to EPA (2006 b). These are called primary standards and secondary standards. In the United States of America, EPA sets primary standards to protect public health by limiting the levels of contaminants in drinking water and these primary standards are enforceable under the law. On the other hand,

secondary standards are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discolouration) or aesthetic effects (Such as taste, odour, or colour) in drinking water. In the United States of America, EPA recommends secondary standards to water systems but does not require systems to comply. However, states may choose to adopt them as enforceable standards.

The list of metal contaminants investigated in this study and their Maximum Contaminant Levels (MCL) as presented by EPA (2006b) are shown in Appendix 1. It should however be noted that some of the metals examined in this study are needed for normal healthy living.

2.4. **Fate and Transport of Metal Contaminants in Natural Water**

The metal ions that enter the aquatic environment do not just remain static in it; they undergo some forms of dynamic processes which may be physical or chemical in nature. Metal ions in natural water may be present in the soluble phase, or adsorbed onto the suspended particulates, or bound to the bed sediments. Forstner and Wittmann (1979) observed that, the greater part of the heavy metals transported by natural water system is, under normal physico-chemical conditions, rapidly adsorbed onto particulate material. Similar observation was made by Jenne *et al* (1980) when they

claimed that on a weight basis, trace elements in natural surface waters generally are at least three orders of magnitude more concentrated in the solid phase than in the aqueous phase.

The complex nature of both the suspended and bottom sediments in natural water accounts for the difficulty that lies in understanding the ways in which metals are bound to these sediments. Dossis and Warren (1980) noted that sediments are normally mixtures of several components including different mineral species and organic debris. It has been suggested that heavy metals are associated with the solid phase in aquatic environment by adsorptive bonding, co precipitation by hydrous iron and manganese oxides, complexation by organic molecules, and incorporation in crystalline minerals (Forstner and Wittman, 1979 and Dempsey and Singer, 1980).

Although, most metal ions in natural water are more concentrated in the solid phase than in the aqueous phase, it has been demonstrated that the metal ions immobilized on the solid phase (that is, suspended particulates and bottom sediments) do not necessarily stay in that condition, but may be released as a result of some physico-chemical changes that take place in the aquatic environment (Forstner and Wittmann, 1979). Indeed, metal ions in natural water are constantly being immobilized and remobilized between the

aqueous and the solid phases. At a given physcio-chemical condition, the metal ions are in dynamic equilibrium between the aqueous and the solid phases. The physico-chemical processes that control these immobilization and remobilization processes include among other things; the pH of the aquatic environment at any given time, the presence and concentration of organic complexing agent, the presence of competing ions, the presence and concentration of inorganic anions such as the hydroxide ions, the carbonate and sulphide ions, the ionic strength, the nature of the clay minerals present, the exchange capacity of the available metal ions, and changes in the redox conditions of the aquatic environment (Zemann and Wedepohl, 1970; Brehler and Wedepohl, 1970; Usdowski and Mueller, 1970; Singer, 1977; Benjamin and Leckie, 1980; and Dempsey and Singer, 1980).

The importance of the factors that control the sorption and the desorption of metals on the solid phase in natural water system cannot be overemphasized if one considers the fact that enrichment of the aqueous phase by toxic metals can be significantly enhanced due to slight changes in those factors that favour the desorption process. For instance, Florence (1980) observed that most fresh waters have pH values that are in the critical range for adsorption of many heavy metals on particles. Since as small as a decrease of 0.5pH unit can mean the difference between complete adsorption

and complete desorption, concentration of heavy metals in natural water depend on the pH of the aqueous environment. It has been speculated that the significant increase in fish mortalities reported in 1972 by Beamish and Harvey when soft fresh water lakes were acidified by atmospheric SO_2 pollution may have been partly the result of the release of ionic copper, lead, and other heavy metals from colloidal particles and sediments (Florence, 1980).

2.5. **Metal Speciation in Natural Water**

Speciation, according to Research Group for Atomic Spectrometry (1996), concerns the identification and quantitation of specific forms of an element in environmental or biological samples. It is becoming increasingly apparent that determination of the total concentration of a trace metal provides very little information about its toxicity and bioavailability or its likely behaviour in a natural water system or a water treatment plant (Florence, 1980). Depending on the chemical forms of the metal, water with a high total metal concentration may be less toxic than one with a lower total metal concentration. For instance, determination of the total chromium concentration in two different water systems may provide little information as to the chromium toxicity in the two water systems since Cr^{6+}, which has

been classified as human carcinogen (Barrett and Copeland, 1979), may be present at higher concentration than Cr^{3+} in the water system with a lower total chromium concentration whereas the other water system that have higher total chromium concentration may contain more of Cr^{3+} than Cr^{6+}.

The development of analytical techniques to reliably measure the concentrations of the various chemical forms of a trace metal in a water sample is one of the most challenging problems presently facing analytical chemists. As pointed out by Florence (1980), it was only in about three decades ago that analytical methods have been refined sufficiently to allow total metals to be determined with confidence at the microgram per liter level. The magnitude of the task, according to Florence (1980), is obviously much greater if each total metal measurement must then be divided into the several different chemical forms that contribute to the total.

In recent time, several methods have been employed for the identification and quantification of the different forms in which metals exist in natural water system. Included among these methods are: computational methods, dialysis, ultra filtration, and centrifugation, ion exchange, liquid-liquid extraction, and anodic stripping voltammetry and polarography (Florence, 1980). A method for the determination of different lead species

(alkyl lead species) in environmental samples using gas chromatography coupled with atomic absorption spectrometer has been described by Johansson (1996). In a study conducted by Cordi *et al* (2002) on the analysis of natural water and sediments using electroanalytical methodology, it was discovered that, though fewer metals could be analyzed with voltametric method when compared with atomic absorption spectrometry, the different forms in which those few metals were partitioned in natural water was successfully determined using voltammetric method. Investigations on metal speciation of Pb, Zn, As and Cu in some environmental samples using size and density fractionation, isotopic analysis, X-ray diffraction, X-ray flourecence, scanning electron microscopy and microprobe analysis, chemical sequential extraction, and surface analysis with both X-ray photoelectron spectroscopy and laser ionization have also been conducted (Walker and Associates, 2002).

However, it should be noted that in speciation analysis, removal of the sample from its natural surroundings may induce pronounced chemical and physical changes causing the species distribution to alter. This is so, since in a dynamic system such as natural water system, some disruption of the chemical equilibrium is inevitable. Even the relatively simple act of filtration of the samples may cause a number of unintended changes to occur possibly

leading to filtration-induced artifacts during sample analysis and uncertainty in the results (Puls and Barcelona, 1996). It has also been shown by Florence (1980) that by removing the particulate matter during filtration, alteration in the concentration of dissolved oxygen and carbon dioxide can cause significant changes in the metal speciation. Another source of error in speciation analysis is the contamination of the samples during collection and storage. For instance, Florence (1980) argues that zinc contamination is particularly serious because the element is present in relatively high concentrations in a wide range of materials commonly present in the laboratory. Even, human skin (epidermis) has been shown to be very high in zinc, and a minute flake of skin in an analytical solution can ruin an analysis (Florence, 1980).

2.6 Principle and Applications of Atomic Absorption Spectrometry

Atomic Absorption Spectrometry (AAS) is a common technique for detecting and measuring concentration of metals and metalloids in biological, environmental and geological samples. AAS can be used to analyze the concentration of over 62 different elements in solution (Wikipedia, 2006). An indirect determination of phosphate, silicate and niobium by AAS using chemical amplification procedure has also been described (Thompson and Reynolds, 1978).

According to Royal Society of Chemistry, RSC (2006), atomic absorption spectrometer has the following three components: a light source which is capable of producing light of characteristic wavelength, a device for producing an atomic vapor of the element from the compounds present in the sample solution, and a device for measuring the specific light absorbed. The light source is usually a lamp having a hollow cathode made of the element to be determined. The production of free atoms occurs in an atomizer and the process is called atomization. Most of atomic absorption equipments use flames for the atomization process. Other devices for atomizing the elements in the sample matrix are electrothermal atomizer, carbon rod analyzer and tantalum boat analyzer (Ma and Gonzalez, 1997). A photomultiplier is usually used to measure the amount of light absorbed.

In AAS, a solution containing metallic species is aspirated into a suitable flame and an atomic vapor of the metal will generally be formed. If irradiated with light of their own characteristic resonance wavelength, the ground state atoms will absorb some of the radiation. The absorbance being proportional to the population density of atoms in the flame. From a calibration curve prepared from standard solutions of the element to be determined, the concentration of the element in a sample matrix can be obtained.

CHAPTER THREE

3.0 EXPERIMENTALS

3.1 Description of the Study Area

Azare is located in the Northeast of Bauchi state and is about 250 kilometres from Bauchi town by major road. Azare is located at latitude $11^0$55'N and longitude $10^0$10'E. Its position in the Sudan Savanna climo-vegetative zone gives it a macro-climate regime of a wet season of basically 5 months, and dry season for the rest of the year. The dominant climatic feature of Azare is a wet season which extends from May to September and seven months of dry season from October to April. Mean monthly temperature of Azare ranges from a low value of 20.10^0C in December and January to a high value of 32.50^0C in April and May (Shehu, 2000).

Azare is located on the border of two types of geologic units. Aeolian sands of the Chad formation occurring to the North of Azare and continental sand stones with grits and clay chiefly of the keri-keri formation occurring to the south of Azare (Shehu, 2000).

As pointed out earlier, the population of Azare is over 150 thousand. The major land uses in Azare as pointed out by Ishiaku (2000) include farming and animal rearing, residential, educational, governmental, commercial, recreational, health and transportation.

Appendices II, III and IV show the geographical map of Bauchi state showing the location of Azare – the study area, the description of the sampling sites for bore-holes, and the description of the sampling sites for well respectively.

3.2 Materials and Reagents

3.2.1 Materials Required

The following materials in addition to other common laboratory materials were used for the experiment described in this chapter

1. UNICAM 969 AA Spectrometer
2. 0.45 μm filter membrane

3.2.2 Reagents Required

The following reagents were used in carrying out the experiment described in this chapter.

1. 0.2% (v/v) HNO_3 solution: This was prepared in $1dm^3$ volumetric flask by dissolving $2cm^3$ of concentrated HNO_3 in distilled water and then made up to volume using distilled water.
2. Concentrated hydrochloric acid (HCl)
3. Concentrated nitric acid (HNO_3)
4. Distilled water

5. 0.4% (w/v) Lanthanum chloride solution: This was prepared in 1dm^3 volumetric flask by dissolving 4g of lanthanum chloride in water and then made up to volume using distilled water.
6. 20%(w/v) NaOH solution: This was prepared in 1dm^3 volumetric flask by dissolving 200g of NaOH pellets in distilled water and then made up to volume using distilled water.
7. 1% mixture of chelating Agents: This was prepared in 1dm^3 volumetric flask by dissolving 10g of Ammonium pyrolidine dithiocarbamate (APDC) and 10g of Diethylammonium diethyldithiocarbamate (DDDC) in distilled water and then made up to volume using distilled water.
8. Methylisobutyl ketone (MIBK)
9. Buffer solution: Prepared by mixing the appropriate amounts of citric, boric, and phosphoric acids in water to give a solution that is 0.5M in each acid.
10. 1000mg/L stock solution of potassium: This was prepared in 100 cm^3 volumetric flask by dissolving 0.191g potassium chloride in distilled water and the solution diluted to 100 cm^3 using distilled water.

11. 1000mg/L stock solution of calcium: This was prepared in 100 cm^3 volumetric flask by dissolving 0.250g of calcium carbonate in 50 cm^3 of 1:3 HCl solution and diluted to volume with distilled water

12. 1000mg/L stock solution of magnesium: This was prepared in 100 cm^3 volumetric flask by dissolving 0.100g of magnesium metal in 50 cm^3 solution of 1.1 HNO_3 solutions and the resulting solution diluted to volume using distilled water.

13. 1000mg/l stock solution of copper: This was prepared in 100 cm^3 volumetric flask by dissolving 0.100g of copper metal in 50ml 1:1 HNO_3 solution and the resulting solution diluted with distilled water.

14. 1000mg/L stock solution of Zinc: This was prepared in 100 cm^3 volumetric flask by dissolving 0.100g of zinc metal in 50ml 1:1 HNO_3 solution and the resulting solution diluted with distilled water.

15. 1000mg/L Stock solution of Manganese: This was prepared in 100 cm^3 Volumetric flask by dissolving 0.100g of manganese metal in 50 cm^3 1:1 HNO_3 solution and the resulting solution diluted with distilled water.

16. 1000mg/L stock solution of Lead: This was prepared in 100 cm^3 volumetric flask by dissolving 1.599g of lead nitrate in 1% HNO_3 solution and the resulting solution diluted to with distilled water.
17. 1000mg/L stock solution of cadmium: This was prepared in 100 cm^3 volumetric flask by dissolving 0.100g of cadmium metal in 1:1 HNO_3 solution and the resulting solution diluted using distilled water.

3.3 Collection and Preservation of Samples

3.3.1 Collection of Samples

A total of eighty (80) groundwater samples, each with a volume of about one litre (1L), were collected from forty (40) sampling sites within Azare town. The forty sampling sites comprise of twenty boreholes (BH_1 to BH_{20}) and twenty hand-dug wells (W_1 to W_{20}) which were randomly selected for the study. Two samples were collected from each sampling site. One of the samples from each sampling site was used for total metal determination while the other one was used for dissolved metal determination.

3.3.2 Preservation of Samples

All the eighty samples collected were stored in plastic sample bottles at the point of collection. Samples collected for total metal determination (samples A_1 to A_{40}) were immediately preserved by adding 0.2% HNO_3

solution to bring the pH below 2. All samples were immediately transported to the laboratory where they were stored at a temperature of about 4^0C in a refrigerator. The preservation step described above was carried out in order to stop, or at least slow down, some of the chemical and biological processes which may bring about changes in the compositions of the analytes in the samples (Goulden, 1978).

Samples used for dissolved metal determination (samples B_1 to B_{40}) were not preserved prior to filtration procedure as changes in pH significantly affect the equilibrium concentration of metals between the soluble phase and the suspended phase in water (Benjamin and Leckei, 1980).

3.4 Preparation of Samples

3.4.1 Filtration Procedure

The forty (40) samples that were meant for dissolved metal determinations were filtered using 0.45μm filter membranes.

3.4.2 Digestion Procedure

100ml portions were measured from samples A_1 to A_{40} and samples B_1 to B_{40}, and transferred into clean beakers. These 100ml portions were taken twice from each sample, making the total number of sub-samples to be

160. Each of these 160 sub-samples was subjected to digestion procedure. Detail of this digestion procedure as described by Van Loon (1980) is given below:

100ml of each sub-sample was placed in a beaker and 1ml of nitric acid was added to it. This acidified sub-sample was then evaporated to dryness on medium heat on a hot plate, 2ml of HCl and 1ml of HNO_3 added and the resulting solution evaporated to dryness. Then, one drop of HCl was added and the resulting solution was diluted to 100ml with distilled water.

3.4.3 Preparation of Samples for Potassium, Calcium and Magnesium Determination

Eighty out of the digested sub-samples, comprising of 40 unfiltered (samples A_1 to A_{40}) and 40 filtered (B_1 to B_{40}) samples from the 40 sampling sites were used for the determination of potassium, calcium and magnesium. To each of these 80 sub-samples, 10ml of 0.4% lanthanum chloride solution was added. This step is required to ensure that chemical interference due to the presence of phosphate in the matrix solution is overcome during the determination of Ca (Thompson and Reynolds, 1978). These 80 sub-samples were then stored in plastic containers for potassium, calcium and magnesium determination.

3.4.4 Preparation of Samples for Heavy Metals Determination

The remaining 80 digested sub-samples which comprise of 40 unfiltered (A_1 to A_{40}) and 40 filtered (B_1 to B_{40}) samples from the 40 sampling sites were subjected to complexation and extraction procedures as described by Van Loon (1980) and Goulden (1978).

In this procedure, 100ml of each of the digested sub-samples was transferred into a 250ml separatory funnel. 4ml of the buffer solution was then added to bring the pH to 4.0± 0.1. The pH was adjusted by adding sufficient 20% NaOH solution. 5ml of 1% chelating agents (mixture of APDC and DDDC) was then added to the resulting buffered solution. The resulting solution was shaken briefly and 10ml of MIBK was added. The mixture was shaken vigorously for 2 minutes. The layers were then allowed to separate and the aqueous (lower) layer discarded while the MIBK (upper layer) was retained and stored in a capped glass bottle.

3.5 Preparation of Standard Solution and Reagent Blanks.

3.5.1 Preparation of Standard Solutions for Potassium, Calcium and Magnesium

Appropriate volumes of the stock standard solutions for K, Ca and Mg were transferred into five 100ml volumetric flasks and these were diluted to

give the ranges of concentrations shown in Appendices V, VI and VII for K, Ca and Mg respectively. These standard solutions were treated the same way that the test solutions meant for K, Ca and Mg determinations were treated.

3.5.2 Preparation of Standard Solutions for the Heavy Metals

Complex standard solutions that approximately matched the constitution of the test solutions that were meant for heavy metals determination were prepared. Thompson and Reynolds (1978) favour the use of complex standard solution for many analyses because the problems associated with chemical interferences are overcome and the procedure also reduces the number of separate standard solutions required.

In this procedure, appropriate volumes of the stock standard solutions for Cu, Zn, Mn, Pb and Cd were transferred into a 100ml volumetric flask. The content of this flask was then diluted to give the first standard solution for each of the heavy metals. The procedure was repeated to prepare the complex standard solutions for the heavy metals in additional four separate volumetric flasks. Details of the concentration ranges for all the heavy metals investigated in this study are shown in Appendices VIII, IX X, XI, and XII.

The buffering, complexation and extraction into MIBK carried out for each of the complex standard solution as described for the test solutions in sub-section 3.4.4 above.

3.5.3 Preparation of Reagent Blank

Two reagent blanks, one for K, Ca and Mg and the other for heavy metals were prepared. The first reagent blank contained all the reagents used in the preservation and preparation of samples and standard solutions for K, Ca and Mg determination while the second reagent blank contained all the reagents that were used in the preservation and preparation of samples and standard solutions for heavy metals determination.

3.6 Analytical Techniques

3.6.1 Preparation of Calibration Curves

The standard solutions prepared for each metal were aspirated into the flame system of the atomic absorption spectrometer and the absorbance corresponding to the concentration in each standard solution measured. These absorbances were plotted against the concentrations of metal in the various standard solutions. The calibration curves obtained for K, Ca, Mg, Cu, Zn, Mn, Pb and Cd are shown in Appendices XIII, XIV, XV, XVI, XVII, XVIII, XIX, and XX respectively.

3.6.2 Determination of Metal Concentrations in the Samples.

To determine the concentration of each metal contaminant in the samples, the blank reagent was first aspirated into the flame system of the AA spectrometer and the absorbance measured. Thereafter, the absorbance of each sample solution was measured in a similar manner and the concentration of the particular metal obtained from the calibration curve corresponding to the particular metal under determination. This was done by interpolation on the calibration curve with the aid of computer coupled with the atomic absorption spectrometer.

3.7 Method of Data Analysis

The data obtained from this investigation were treated using simple ratio, simple percentage, and t-test statistics. Appendix XXI shows the formula for computing F test while Appendices XXII and XXIII show the formulas for computing t-tests when the variances are assumed to be unequal and when the variances are assumed to be equal respectively. (Bluman, 1998).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results of Total Concentrations of Metal Contaminants in Azare Groundwater System

The concentrations of total metals in all the boreholes and wells investigated in this study are shown in Appendices XXIV and XXV respectively. The results presented in Appendices XXIV and XXV are summarized as mean concentrations, standard deviations and range values of the total metal contaminants in Tables 1 and 2 respectively.

The result in Table 1 indicates that the total concentrations of K, Ca and Mg in the water samples from boreholes investigated were in the range of 0.1244 to 1.0824mg/L, 0.3350 to 0.9025mg/L, and 0.1307 to 0.6709mg/L respectively. The concentrations of K, Ca and Mg (expressed as mean ± standard deviation) were 0.3233 ± 0.2455mg/L, 0.5433 ± 0.1762mg/L, and 0.3178 ± 0.1641mg/L respectively (see Table 1).

The result in Table 1 also indicates that the total concentrations of Cu, Zn, Mn, Pb and Cd in the water samples from the boreholes investigated ranged from 0.0461 to 0.6431mg/L, 0.0960 to 1.4894mg/L, 0.0534 to 0.4310mg/L, 0.0438 to 0.7337mg/L, and ND to

0.0110mg/L respectively. The mean concentrations of the total Cu, Zn, Mn, Pb and Cd in the boreholes investigated in this study (expressed as mean ± standard deviation) were 0.2386 ± 0.1361mg/L, 0.3260 ± 0.3187mg/L, 0.1879 ± 0.1082mg/L, 0.1234 ± 0.1480mg/L, and 0.0049 ± 0.0037mg/L respectively (see Table 1).

The distribution pattern of metal contaminants of water samples collected from the boreholes investigated in this study (on the basis of the mean concentrations) followed the order: Ca > Zn > K > Mg > Cu > Mn > Pb > Cd (see Table 1).

The result in Table 2 indicates that the total concentrations of K, Ca and Mg in the water samples from the hand-dug wells investigated were in the range of 0.3082 to 2.7262mg/L, 0.3917 to 5.1730mg/L, and 0.1704 to 4.0780mg/L respectively. The concentrations of K, Ca and Mg (expressed as mean ± standard deviation) were 0.8790 ± 0.6823mg/L, 1.1923 ± 1.1337mg/L, and 0.9543 ± 1.0186mg/L respectively (see Table 2).

The result in Table 2 also indicates that the total concentrations of Cu, Zn, Mn, Pb and Cd in the water samples from the hand-dug wells investigated ranged from ND to 0.4390mg/L, 0.0535 to 0.3217mg/L, 0.0442 to 0.6313mg/L, 0.0245 to 0.1966mg/L, and ND to

0.0105mg/L respectively. The mean concentrations of the total Cu, Zn, Mn, Pb and Cd in the hand-dug wells investigated in this study (expressed as mean ± standard deviation) were 0.0953 ± 0.1083mg/L, 0.1890 ± 0.0791mg/L, 0.1645 ± 0.1238mg/L, 0.0965 ± 0.0491mg/L, and 0.0041 ± 0.0034mg/L respectively (see Table 2).

The distribution pattern of metal contaminants in the water samples collected from the hand-dug wells investigated in this study (on the basis of mean concentrations) followed the order: Ca > Mg > K > Zn > Mn > Cu > Pb > Cd (see Table 2).

The results obtained in this study show some levels of agreement with the concentrations of total metals in groundwater samples reported by other investigators somewhere else. For instance, Soylak and Elci (2000) reported that the levels of Cu, Pb and Cd in the drinking water from wells and storage tanks in Turkey were in the range of 0.0020 to 0.0216mg/L, 0.0027 to 0.0299mg/L, and 0.0007 to 0.0031mg/L respectively. Similarly, Musa et.al (2004) reported that the concentrations of Pb in well and boreholes water in Zaria, Nigeria ranged from 0.000786 to 0.0595mg/L. Values as high as 4.2mg/L for Zn and 1.4mg/L for Zn have been found in groundwater samples around the mining areas of New Brunswick (Leybourn et.al, 2002).

Ranges of total trace metals in groundwater samples collected in Ottawa County, USA in 1981 as reported by USGS (2003) were from 0.0004 to 0.1330mg/L for Cd, 0.0012 to 0.1230mg/L for Cu, 0.0020 to 0.1240mg for Pb, 0.1500 to 9.800mg/L for Mn, and 0.0040 to 252.0mg/L for Zn. The ranges of concentrations of K, Ca and Mg in boreholes waters within Umuahia metropolis, Nigeria were found by Okeke (2000) to be from 3.5 to 100.5mg/L, 15.0 to 72.0mg/L and 5.0 to 15.0mg/L respectively.

Any observed variations in the levels of metal contaminants between the various groundwater samples reported by the different investigators cited above, could be accounted for if due consideration is given to the diversity that exists in the natural and the anthropogenic sources of metal contaminants in different locations reported.

Table 1: Mean Concentrations, Standard Deviations and Range of Values of Total Metal Contaminants in Borehole Waters

Metal Contaminant	Mean Concentration (mg/L)	Standard Deviation	Range (mg/L)
K	0.3233	0.2455	0.1244 – 1.0824
Ca	0.5433	0.1762	0.3350 – 0.9025
Mg	0.3178	0.1641	0.1307 – 0.6709
Cu	0.2386	0.1361	0.0461 – 0.6431
Zn	0.3260	0.3187	0.0960 – 1.4894
Mn	0.1879	0.1082	0.0534 – 0.4310
Pb	0.1234	0.1480	0.0438 – 0.7337
Cd	0.0049	0.0037	ND – 0.0110

Table 2: Mean Concentrations, Standard Deviations and Range of Values of Total Metal Contaminants in Well Waters

Metal Contaminant	Mean Concentration (mg/L)	Standard Deviation	Range (mg/L)
K	0.8790	0.6823	0.3082 – 2.7262
Ca	1.1923	1.1337	0.3917 – 5.1730
Mg	0.9543	1.0186	0.1704 – 4.0780
Cu	0.0953	0.1083	ND – 0.4390
Zn	0.1890	0.0791	0.0535 – 0.3217
Mn	0.1645	0.1238	0.0442 – 0.6313
Pb	0.0965	0.0491	0.0245 – 0.1966
Cd	0.0041`	0.0034	ND – 0.0105

4.2 Comparison of Total Heavy Metal Concentrations with their Maximum Contaminant Levels in Drinking Water

Figures 1 and 2 are the frequency polygons for comparing the total concentrations of copper in water samples from boreholes and hand-dug wells respectively with the Maximum Contaminant Level (MCL) for Cu in drinking water (1.3mg/L). As shown in Figure 1, all the water samples collected from the boreholes investigated in this study contained total Cu concentrations below the MCL for Cu in drinking water. Similarly, Figure 2 also reveals that all the water samples obtained from hand-dug wells investigated in this study contained total Cu concentrations below the MCL for Cu in drinking water. The implication of this finding is that, Azare groundwater system is safe for drinking as far as the presence of copper in the groundwater system is concerned.

The frequency polygons, comparing the total Zn concentrations in water samples from boreholes and hand-dug wells with the MCL for Zn in drinking water (5.0mg/L) are shown in Figures 3 and 4 respectively. As Figures 3 and 4 revealed, the total Zn concentrations in the water samples from boreholes and hand-dug wells were below the MCL for Zn in drinking water. This implies that both the boreholes and hand-dug wells in Azare groundwater system are safe as far as the contamination of Zinc in the drinking water is concerned.

In Figures 5 and 6, the total Mn concentrations in water samples obtained from boreholes and hand-dug wells were respectively compared with the MCL for Mn in drinking water (0.05mg/L). As shown in Figure 5, total Mn concentrations in the water samples collected from all the boreholes investigated in this study exceeded the MCL for Mn in drinking water. Figure 6 also indicates that the total Mn concentrations in nineteen water samples collected from the hand-dug wells investigated contained Manganese at concentrations higher than the MCL for Mn in drinking water. In other words, it can be said that 95% of the well water samples contained Mn concentrations above the MCL for manganese in drinking water. The implication of the above finding is that Azare groundwater system is not safe for drinking because of the serious manganese contamination.

In Figures 7 and 8, the MCL for Pb in drinking water (0.015mg/L) was compared with the results obtained for the total concentrations of Pb in water samples collected from the boreholes and hand-dug wells investigated in this study respectively. Both Figures 7 and 8 reveal that, lead exceeded the MCL for Pb in drinking water in all the water samples investigated. The implication of the above finding is that, Azare groundwater system is unsafe as far as the contamination of the drinking water by lead is concerned.

The MCL for Cd in drinking water (0.005mg/L) was compared with the total concentrations of Cd in water samples collected from boreholes and hand-dug wells investigated in this study (see Figures 9 and 10 respectively). As revealed in Figure 9, the total Cd concentrations exceeded the MCL for Cd in nine out of the twenty borehole water samples investigated. This corresponds to 45% of the total boreholes investigated in this study. Similarly, the total Cd concentrations in well water samples investigated, as shown in Figure 10, exceeded the MCL for Cd in only seven out of the twenty well water samples investigated. This corresponds to 35% of the well water samples investigated in this study.

Previous investigation on the groundwater system in Eastern Iowa, USA by Sadorf and Linhart (2000) revealed that the concentrations of iron and manganese exceeded the Maximum Contaminant Levels for these metals in drinking water in 53% and 50% respectively of the samples studied. Pelig-Ba et.al (2004) also showed in a study conducted on the trace metal concentrations in borehole waters from the Upper Regions and the Accra Plains of Ghana that, while the concentrations of cadmium, manganese and copper fell below the WHO limits, values for lead and chromium exceeded the WHO limits for drinking water in the areas studied.

Similar studies conducted in various parts of Nigeria also showed that the quality of groundwater has been affected by trace metal contamination. For instance, Aiyesanmi et.al (2004) discovered that the levels of heavy metals in groundwater samples within Okitipupa, Nigeria showed varying concentrations ranging between values below and above the WHO guideline values for drinking water. It has also been shown that the concentrations of lead and iron in drinking water samples hand-dug wells in Onitsha metropolitan areas of Nigeria exceeded the WHO maximum acceptable threshold for these metals (Efe, 2005). The level of lead in water samples collected from hand-dug wells and boreholes in Zaria, Nigeria was found to exceed the WHO drinking water guideline limit in 91% of the samples analyzed (Musa et.al, 2004).

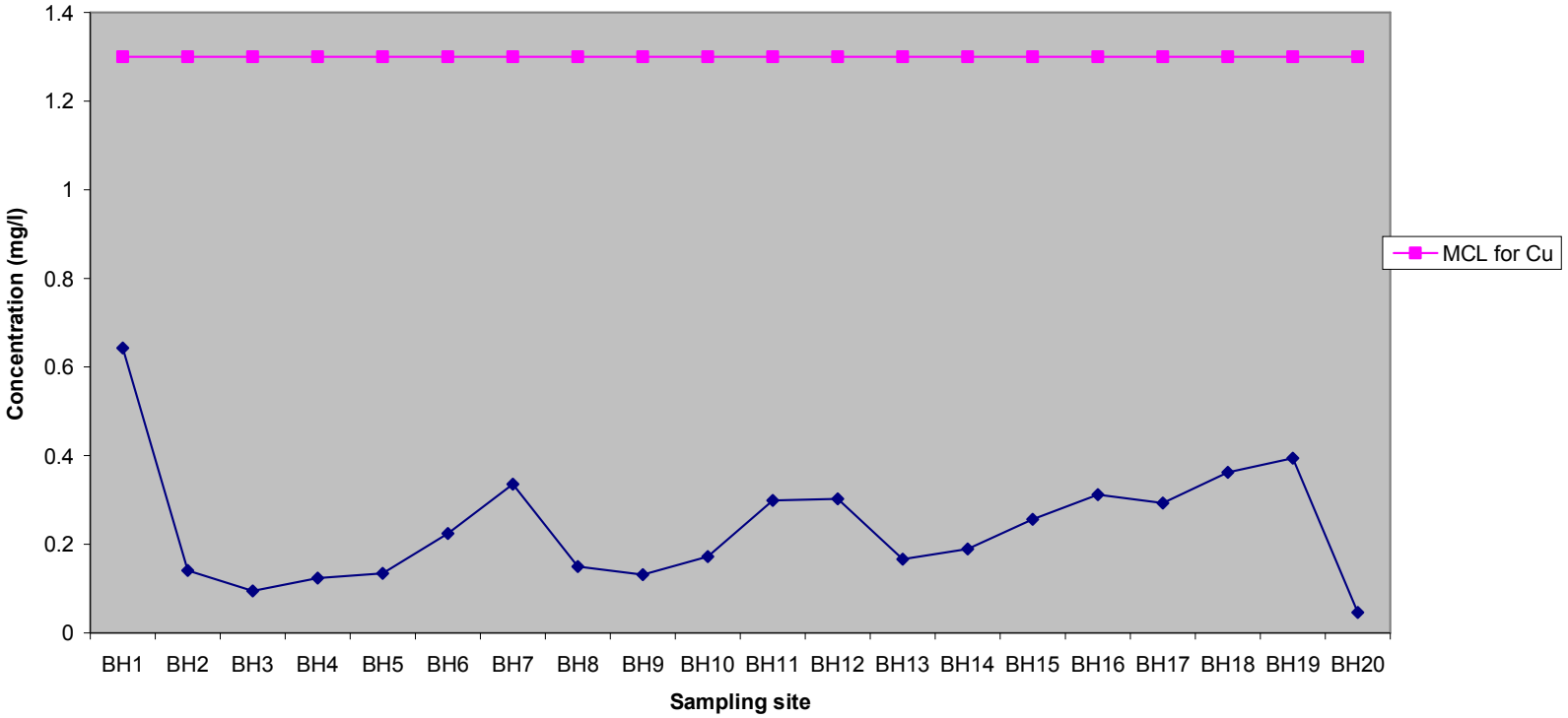

Figure 1: Comparisonn of Total Copper Concentrations in Boreholes with the MCL for Copper in Drinking water

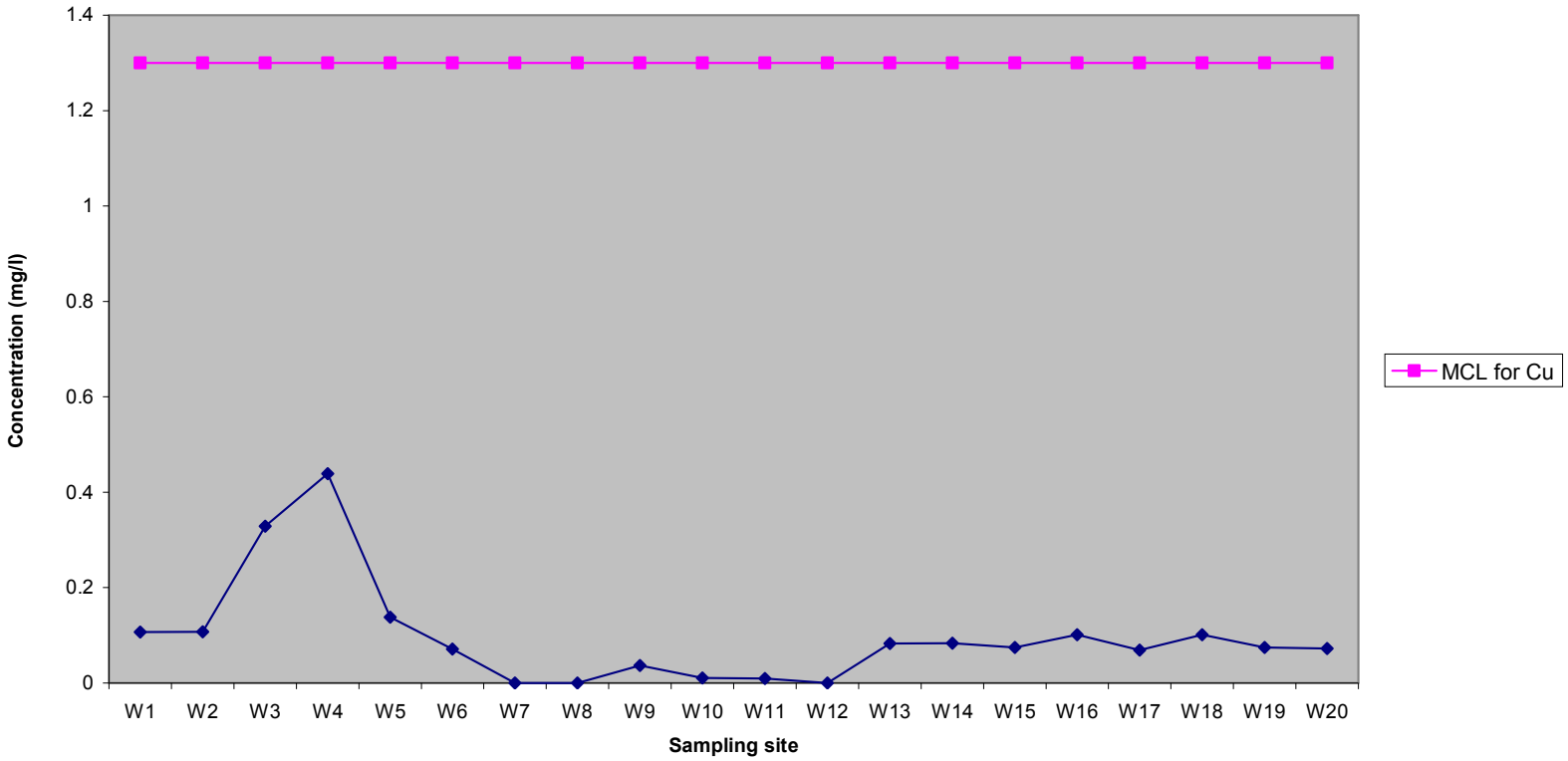

Figure 2: Comparison of Total Copper Concentrations in Wells with the MCL for Copper in Drinking water

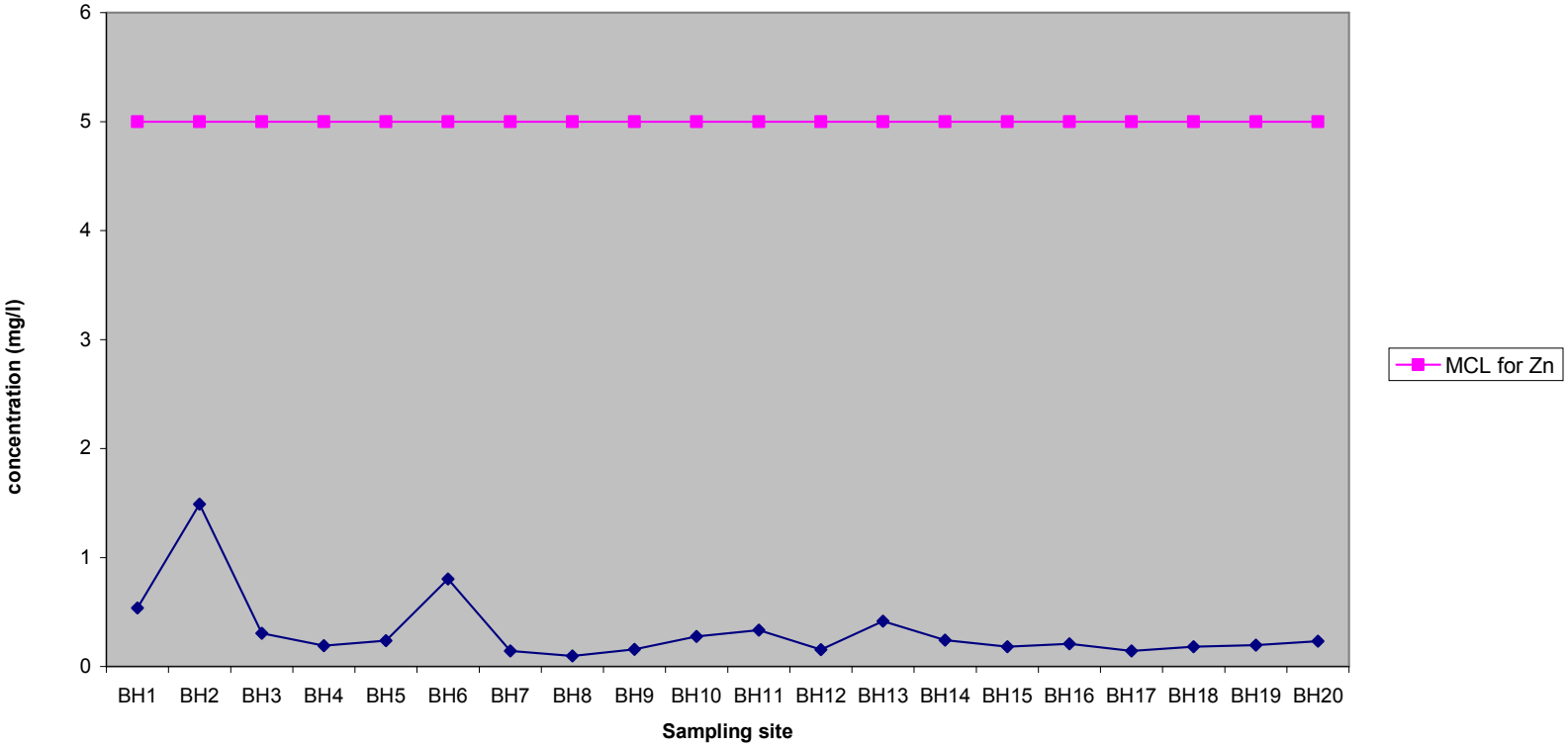

Figure 3: Comparison of Total Zinc Concentrations in Boreholes with the MCL for Zinc in Drinking water

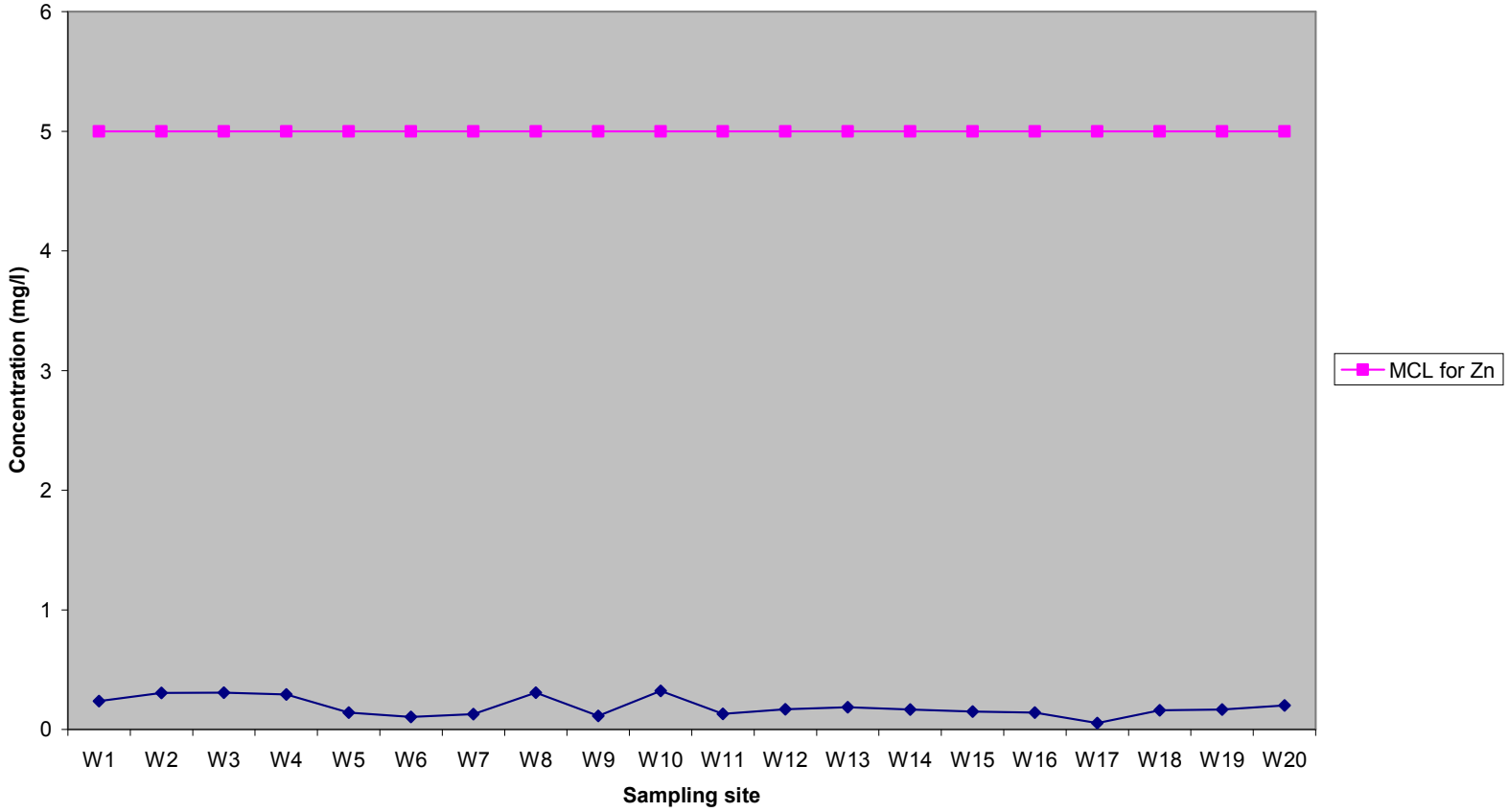

Figure 4: Comparison of Total Zinc Concentration in Wells with the MCL for Zinc in Drinking water

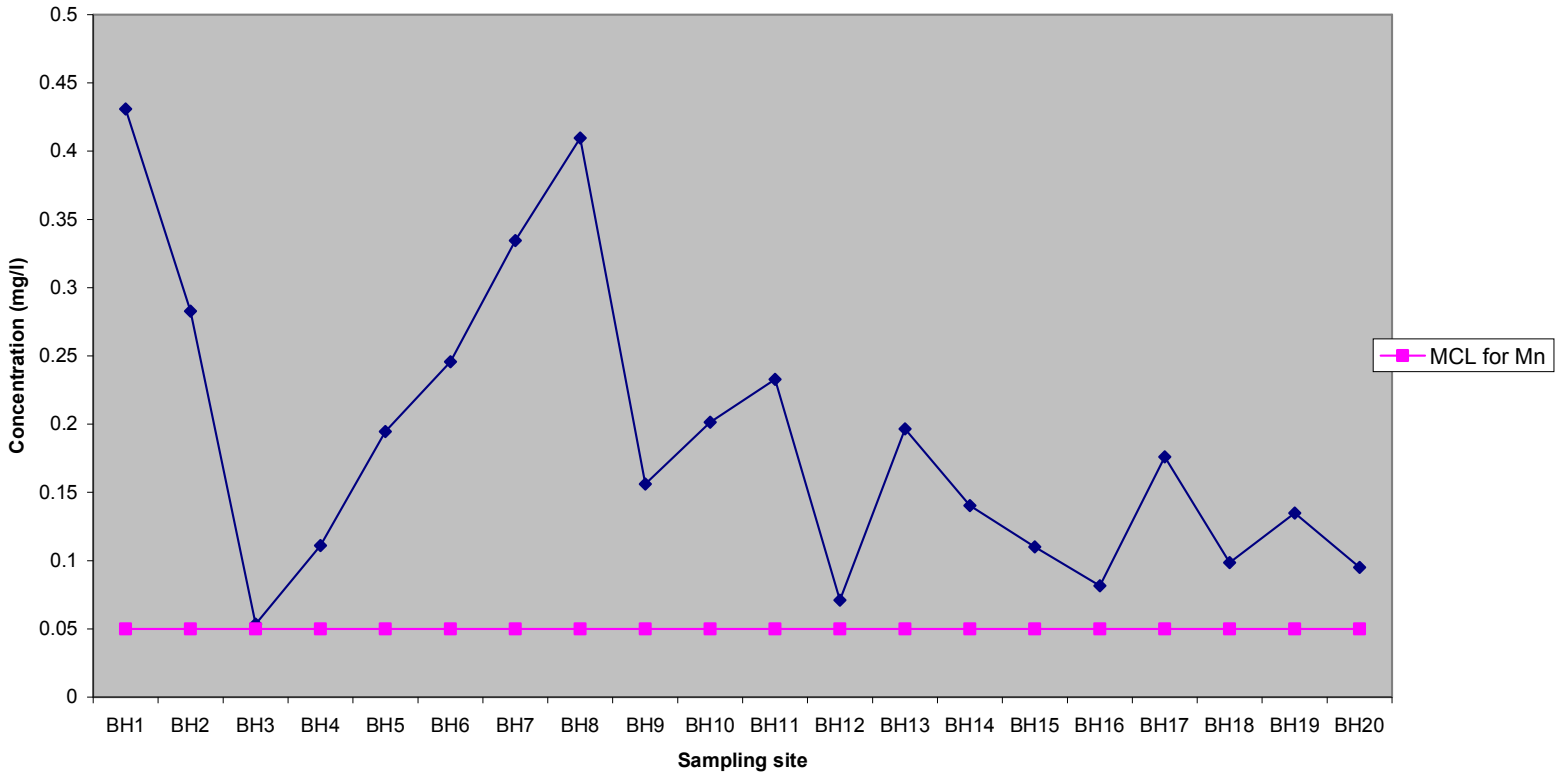

Figure 5: Comparison of Total Manganese Concentrations in Boreholes with the MCL for Manganese in Drinking water

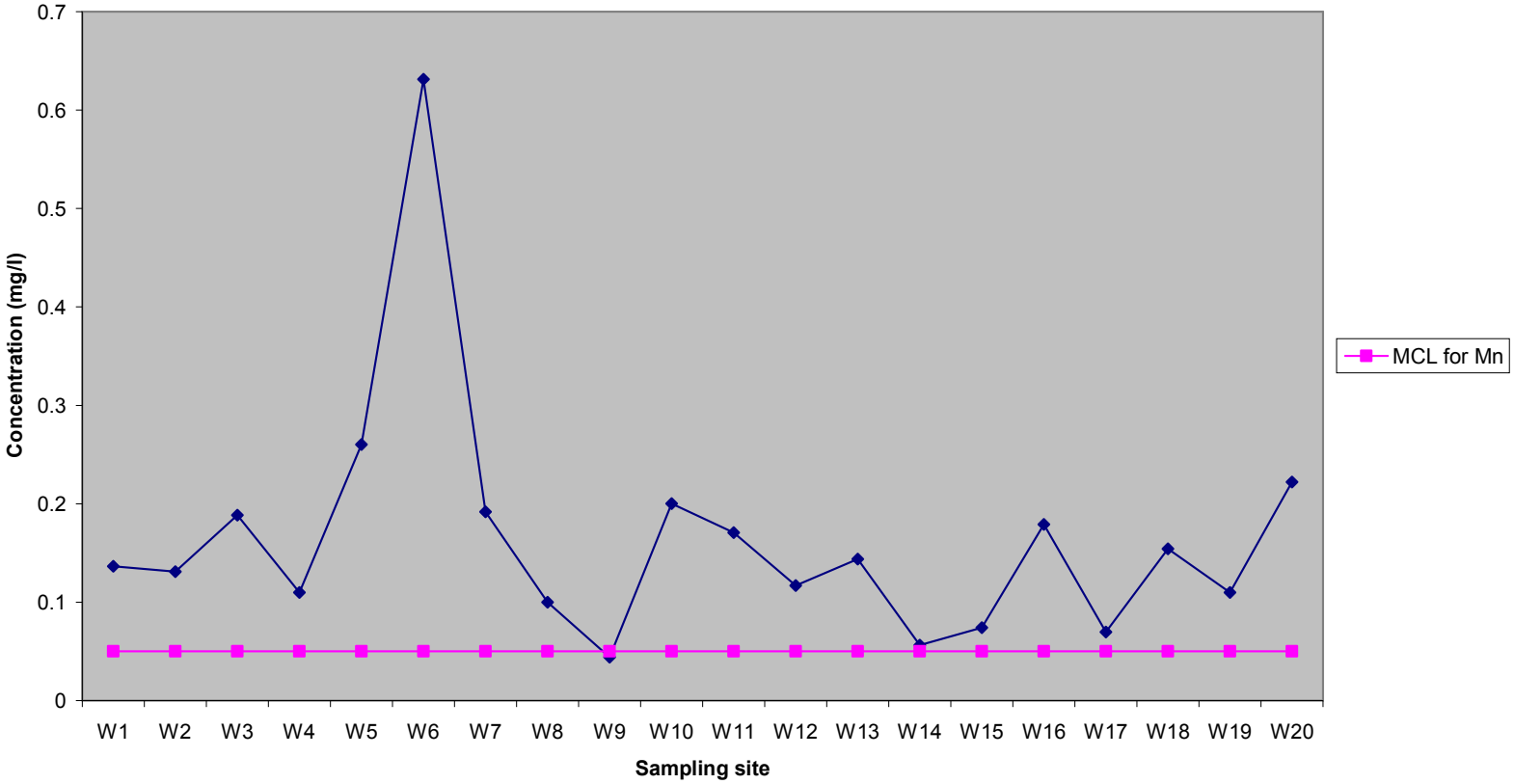

Figure 6: Comparison of Total Manganese Concentrations in Wells with the MCL for Manganese in Drinking water

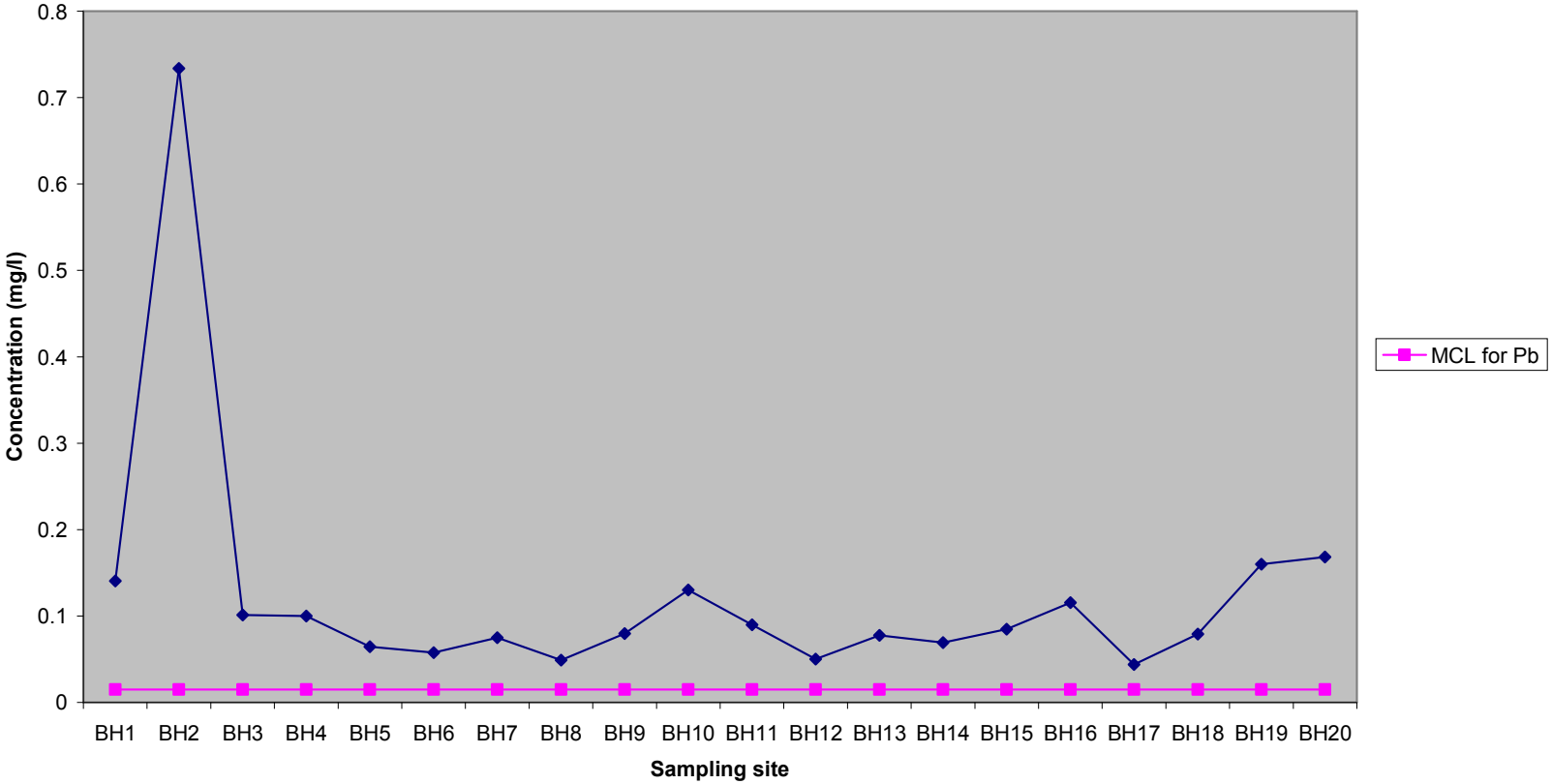

Figure 7: Comparison of Total Lead Concentrations in Boreholes with the MCL for Lead in Drinking water

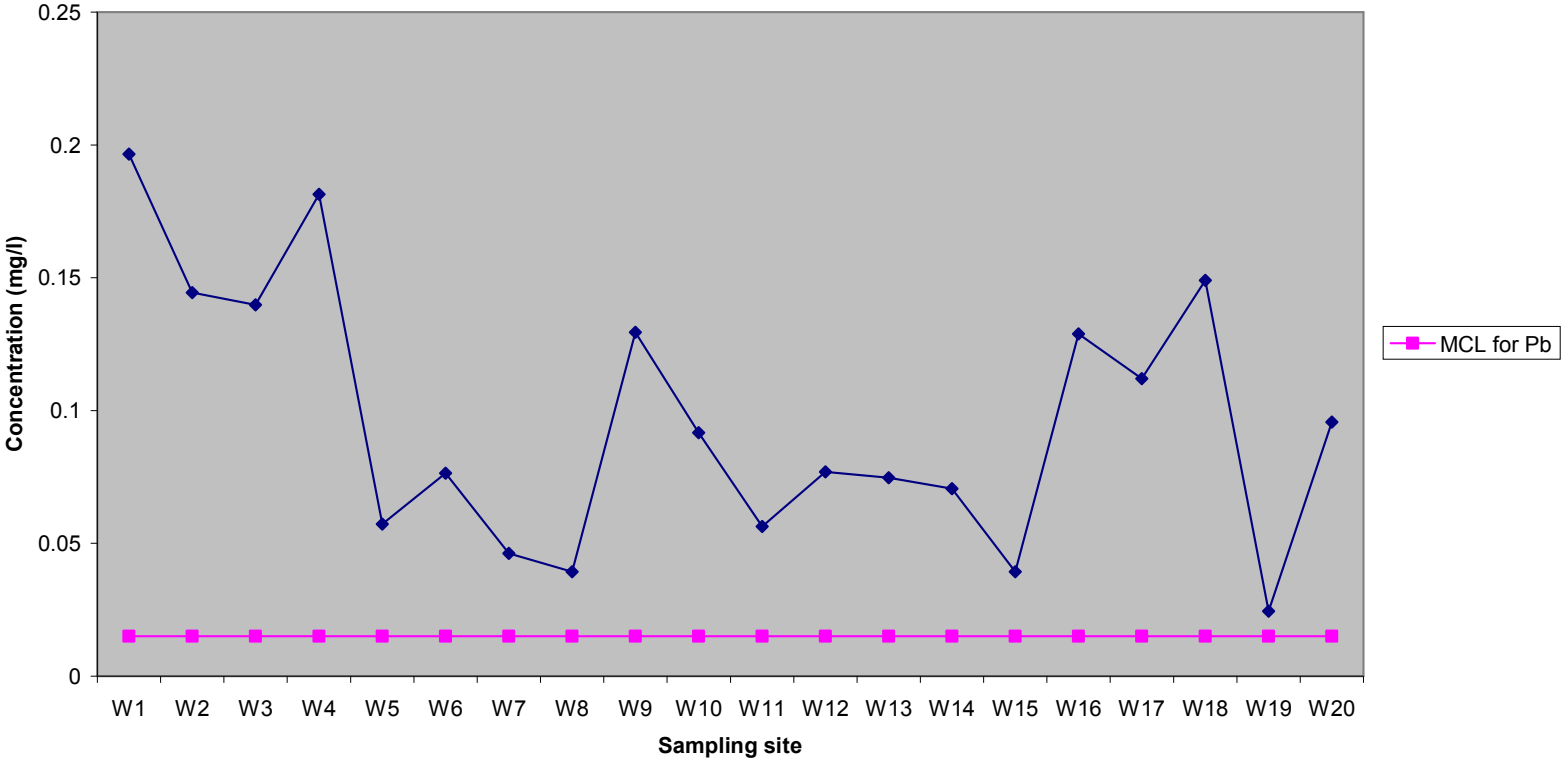

Figure 8: Comparison of Total Lead Concentrations in Wells with the MCL for Lead in Drinking water

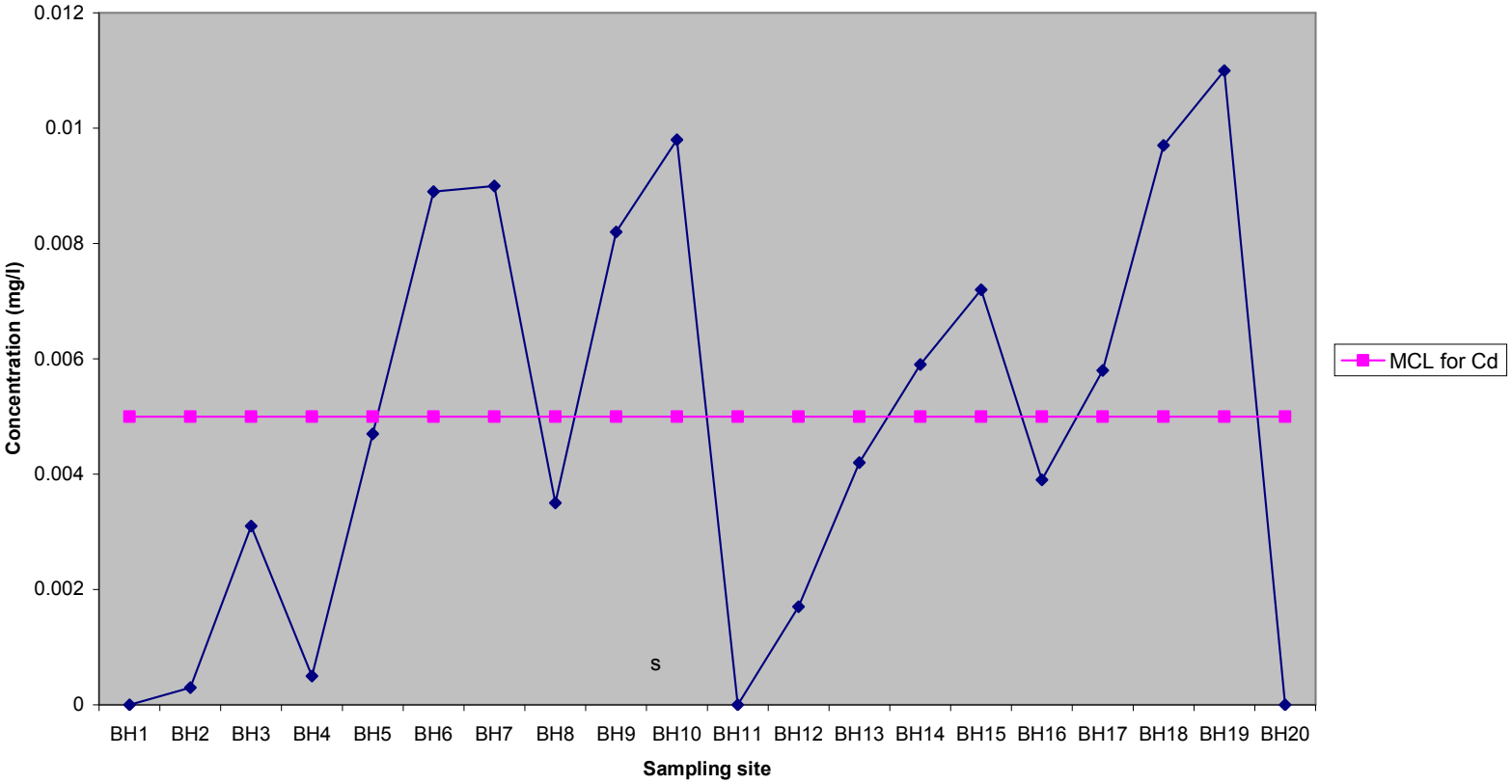

Figure 9: Comparison of Total Cadmium Concentrations in Boreholes with the MCL for Cadmium in Drinking water

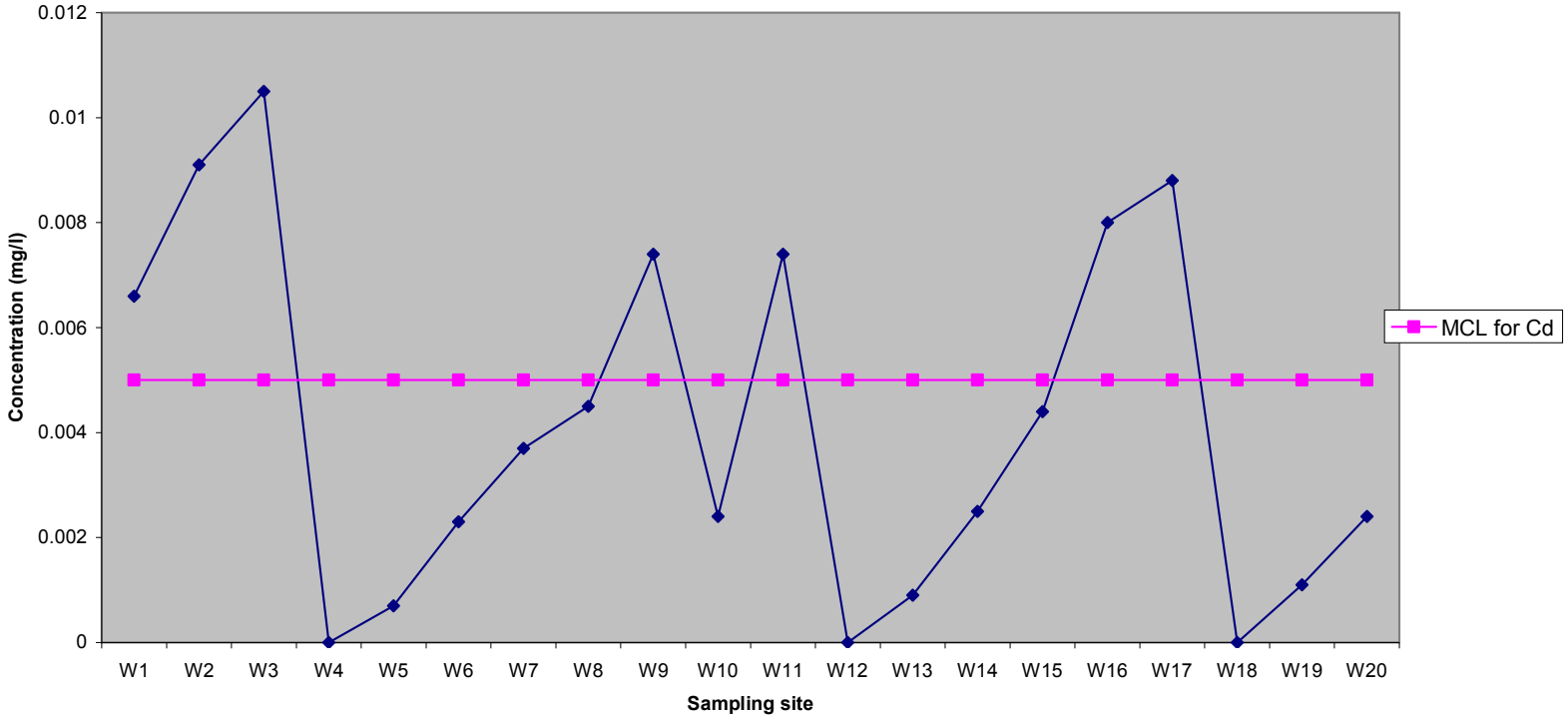

Figure 10: Concentration of Total Cadmium Concentrations in Wells with the MCL for Cadmium in Drinking water

4.3 Comparison of Mean Concentrations of Total Metal Contaminants in Boreholes and Hand-Dug Wells

The mean total concentrations of potassium, calcium, magnesium, copper, zinc, manganese, lead, and cadmium in boreholes and hand-dug wells were compared using t-test statistics (see Tables 3, 4, 5, 6, 7, 8,9, and 10 respectively). As shown in Table 3, the calculated t-test value (3.427) is greater than the critical t-test value (2.861). This implies that the null hypothesis formulated in section 1.3 of this thesis is rejected for potassium. That is, at 0.01 level of significance, there is a significant difference between the mean concentrations of total potassium in boreholes and hand-dug wells.

The calculated t-test value (2.530) for comparing the total calcium concentrations in boreholes and hand-dug wells is lower than the critical t-test value of 2.861 (see Table 4). On the basis of this statistical result, the null hypothesis formulated in section 1.3 is accepted for calcium. That is, there is no significant difference between the mean concentrations of total calcium in boreholes and hand-dug wells investigated at 0.01 level of significance. Similarly, the result of t-test statistics shown in Table 5 indicates that the calculated t-test value (2.759) is less than the critical t-test value (2.861). On the basis of this result, the null hypothesis formulated in section 1.3 is accepted for magnesium. That is, there is no significant difference between the mean

concentrations of total magnesium in boreholes and hand-dug wells investigated at 0.01 level of significance.

Table 6 indicates that the calculated t-test value (3.685) is greater than the critical t-test value (2.576). This implies that the null hypothesis in section 1.3 is rejected for copper. That is, at 0.01 level of significance, there is a significant difference between the mean concentrations of total copper in boreholes and hand-dug wells.

The t-test statistics results shown in Tables 7 and 8 reveal that the calculated t-test values for zinc (1.866) and manganese (0.636) are less than the critical t-test values for these metals (2.861 and 2.576 respectively). On the basis of these results, the null hypothesis in section 1.3 of this thesis is accepted for zinc and manganese. That is, there is no significant difference between the mean total concentrations of zinc and manganese in the boreholes and hand-dug wells investigated in this study at 0.01 level of significance.

Similarly, the t-test statistical results shown in Table 9 and 10 indicate that the calculated t-test values for lead (0.771) and cadmium (0.712) are less than the critical t-test values for these metals (2.861 and 2.576 respectively). On the basis of these results, the null hypothesis formulated in section 1.3 for lead and cadmium is accepted. That is, at 0.01 level of significance, there is no significant difference between the

mean concentrations of total lead and total cadmium in boreholes and hand-dug wells investigated in this study.

The implication of the above findings is that, apart from potassium and copper, the boreholes and the hand-dug wells in Azare groundwater system are similarly affected by metal contamination.

Table 3: Comparison of Total Potassium Concentrations in Bore-holes and Hand-Dug Wells

	N	**Mean (mg/L)**	**Standard deviation**	**Degree of freedom**	**t_{cal} Value**	**$t_{crit.}$ value**	**Level of Significance**
Bore-holes	20	0.3233	0.2455	19	3.427	2.861	0.01
Wells	20	0.8790	0.6823				

Table 4: Comparison of Total Calcium Concentrations in Bore-holes and Hand-Dug Wells

	N	**Mean (mg/L)**	**Standard deviation**	**Degree of freedom**	**t_{cal} Value**	**$t_{crit.}$ value**	**Level of Significance**
Bore-holes	20	0.5433	0.1762	19	2.530	2.861	0.01
Wells	20	1.1923	1.1337				

Table 5: Comparison of Total Magnesium Concentrations in Bore-holes and Hand-Dug Wells

	N	**Mean (mg/L)**	**Standard deviation**	**Degree of freedom**	**t_{cal} Value**	**$t_{crit.}$ value**	**Level of Significance**
Bore-holes	20	0.3178	0.1641	19	2.759	2.861	0.01
Wells	20	0.9543	1.0186				

Table 6: Comparison of Total Copper Concentrations in Bore-holes and Hand-Dug Wells

	N	**Mean (mg/L)**	**Standard deviation**	**Degree of freedom**	**t_{cal} Value**	**$t_{crit.}$ value**	**Level of Significance**
Bore-holes	20	0.2386	0.1361	38	3.685	2.576	0.01
Wells	20	0.0953	0.1083				

Table 7: Comparison of Total Zinc concentrations in Bore-holes and Hand-Dug Wells

	N	**Mean (mg/L)**	**Standard deviation**	**Degree of freedom**	**t_{cal} Value**	**$t_{crit.}$ value**	**Level of Significance**
Bore-holes	20	0.3260	0.3187	19	1.866	2.861	0.01
Wells	20	0.1890	0.0791				

Table 8: Comparison of Total Manganese Concentrations in Bore-holes and Hand-Dug wells

	N	Mean (mg/L)	Standard deviation	Degree of freedom	t_{cal} Value	$t_{crit.}$ value	Level of Significance
Bore-holes	20	0.1879	0.1082	0.636	2.576	2.576	0.01
Wells	20	0.1645	0.1645				

Table 9: Comparison of Total Lead concentrations in Bore-holes and Hand-Dug Wells

	N	**Mean (mg/L)**	**Standard deviation**	**Degree of freedom**	**t_{cal} Value**	**$t_{crit.}$ value**	**Level of Significance**
Bore-holes	20	0.1234	0.1480	19	0.771	2.861	0.01
Wells	20	0.0965	0.0491				

Table 10: Comparison of Total Cadmium concentrations in Bore-holes and Hand-Dug Wells.

	N	**Mean (mg/L)**	**Standard deviation**	**Degree of freedom**	**t_{cal} Value**	**$t_{crit.}$ value**	**Level of Significance**
Bore-holes	20	0.0049	0.0037	38	0.712	2.576	0.01
Wells	20	0.0041	0.0034				

4.4 Distribution of Metal Contaminants between the Soluble and Particulate Phases in Groundwater

The concentrations of soluble metals in all the boreholes and hand-dug wells investigated in this study are shown in Appendices XXVI and XXVII respectively. The results presented in Appendices XXVI and XXVII are summarized as clustered bar charts in Figures 11 and 12 respectively.

Figure 11 shows the average proportions of metal contaminants in the soluble and the particulate phases in water samples collected from the boreholes investigated in this study. As Figure 11 revealed, K, Ca, Mg, Zn and Mn exist predominantly in the soluble phase with the average proportions of these metals in the soluble phase as 84.9%, 80.5%, 88.6%, 67.2% and 56.8% respectively. Also, Figure 11 shows that Cu, Pb and Cd exist predominantly in the particulate phase with the average proportions of these metals in the soluble phase as 22.2%, 39.9% and 17.5% respectively.

The average proportions of metal contaminants in the soluble and the particulate phases in well water samples investigated in this study are shown in Figure 12. The Figure shows that K, Ca, Mg, Zn, Mn exist predominantly in the soluble phase with the average proportions of these metals in the soluble phase as 93.1%, 87.6%, 91.8%, 69.3% and 76.3% respectively. Figure 12 also shows that Cu, Pb and Cd exist

predominantly in the particulate phase with the average proportions of these metals in the soluble phase as 22.5%, 44.5% and 42.5% respectively.

Findings reported from previous study conducted by Yeh (1999) on Erh-Jen estuarine have it that, while Fe, Zn and Cu exist predominantly in truly dissolved phase, Mn and Ni exist predominantly in colloidal phase.

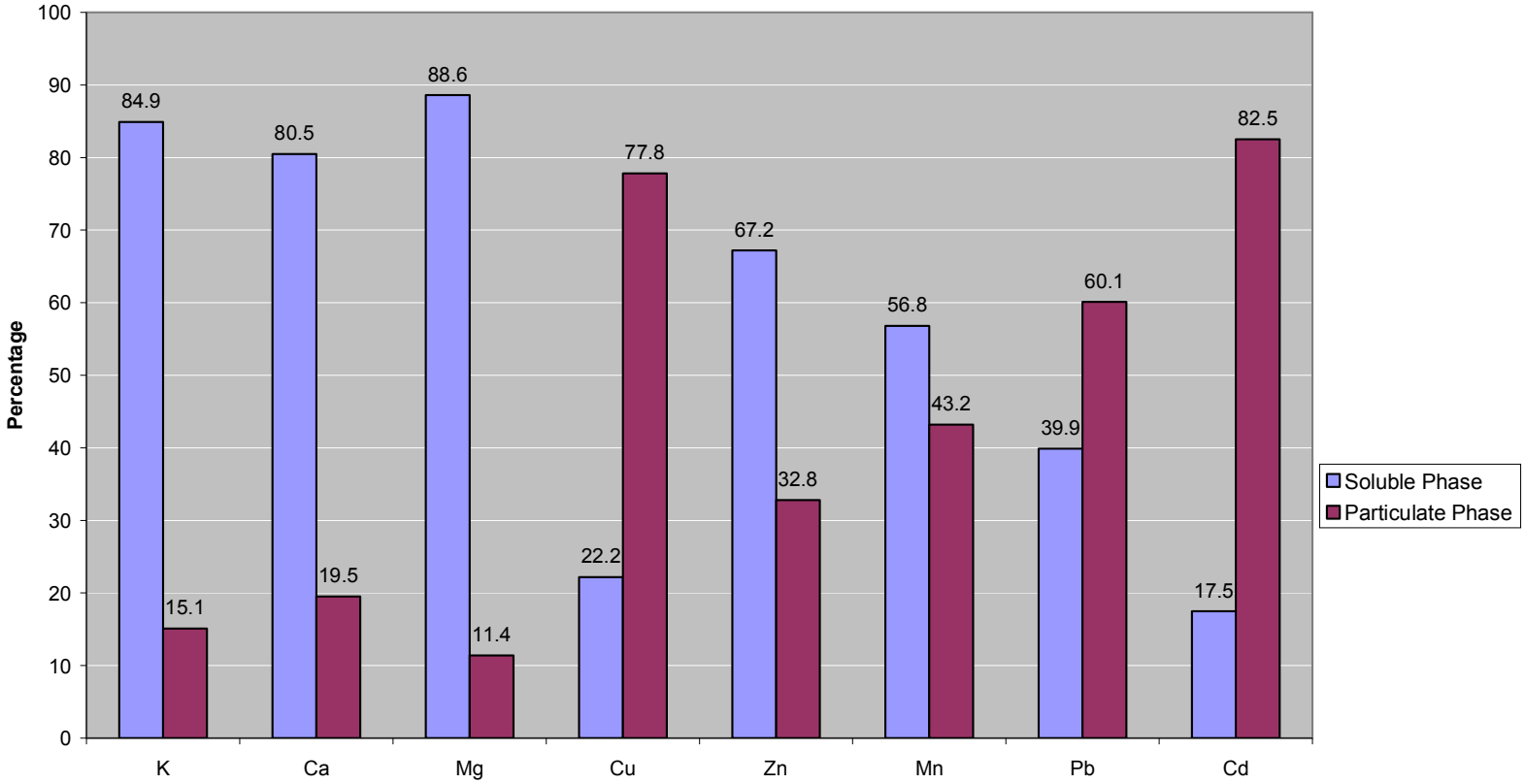

Figure 11: Proportions of Metals Contaminants in the Soluble and Particulate Phases in Boreholes

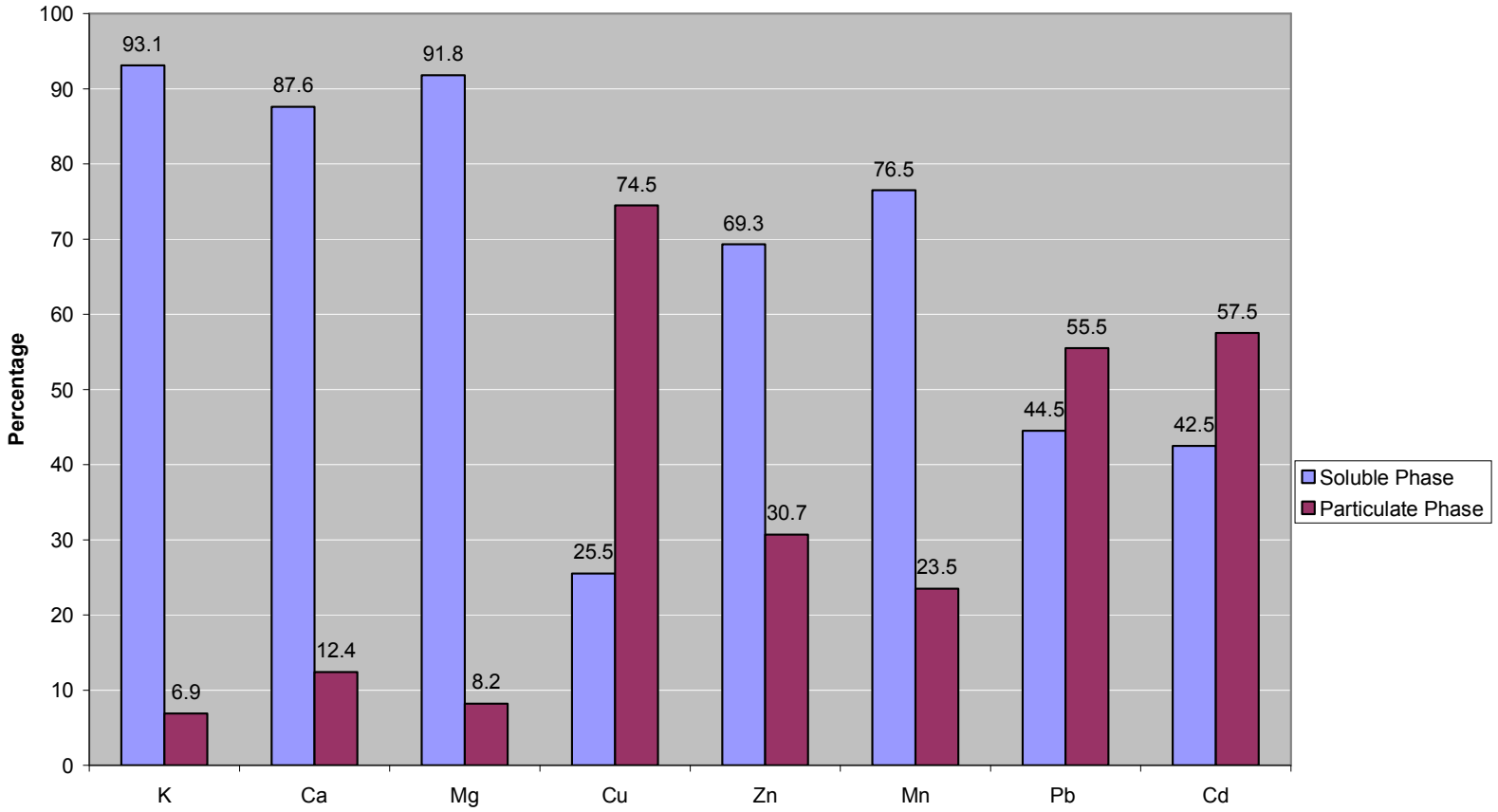

Figure 12: Proportions of Metal Contaminants in the Soluble and Particulate Phases in Wells

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary and Conclusion

This research work aimed at determining the distribution pattern of metal contaminants in Azare groundwater system. In order to achieve this objective, samples were randomly collected from forty sampling sites within Azare town. These sampling sites comprised of twenty bore-holes and twenty hand-dug wells. In each of the sampling sites selected, concentrations of K, Ca, Mg, Cu, Zn, Mn, Pb and Cd were determined in the form of total metals and soluble metals using Flame Atomic Absorption Spectrometric technique. Findings obtained from the study can be summarized as follows;

- Potassium, Calcium and Magnesium were present in all the bore-holes and wells selected for this study. Hence, it can be concluded that Azare groundwater system is a very good source for these nutritional elements.

- The concentrations of total Copper and Zinc were found at levels below the recommended maximum contaminant levels for these metals in the bore-holes and wells investigated in this study. Since Copper and Zinc can be of benefit to human being when they occur

at trace amount in drinking water but may be harmful when they occur at high concentration, it can be concluded that Azare groundwater system is safe for drinking as far as the presence of Copper and Zinc in the groundwater system is concerned.

- The concentrations of Manganese and Lead in water samples from the bore-holes and hand-dug wells selected for this study were found to exceed the maximum contaminant levels recommended for Manganese and Lead in drinking water. From these findings, it can be concluded that Azare groundwater system is not safe for drinking as far as the presence of Manganese and Lead in the groundwater system is concerned.
- Concentrations of Cadmium in the water samples analyzed were found to exceed the maximum contaminant level for Cadmium in drinking water in 45% of the bore-holes and 35% of the hand-dug wells selected for this study.
- No significant differences were found between the levels of Calcium, Magnesium, Zinc, Manganese, Lead and Cadmium in both the bore-holes and wells investigated in this study. It can therefore be concluded that contaminations of bore-holes and hand-dug wells in Azare groundwater system occur at the same rate, as

far as contaminations of Calcium, Magnesium, Zinc, Manganese, Lead and Cadmium are concerned.

- Significant differences were found between the levels of Potassium and Copper in the bore-holes and wells selected for this study. It can therefore be concluded from this finding that the bore-holes and hand-dug wells in Azare groundwater system are not being contaminated at the same rate, as far as contaminations by Potassium and Copper are concerned.
- In all the bore-holes and hand-dug wells investigated in this study, Potassium, Calcium, Magnesium, Zinc, and Manganese were predominantly being transported in the soluble phase while the greater proportion of Copper, Lead and Cadmium were being transported predominantly in the particulate phase.

5.2 Recommendations/Suggestions for Further Study

On the basis of the findings obtained from this study, the following recommendations/suggestions are offered:

- Other physical, chemical and biological parameters should be determined in Azare groundwater system with a view to assessing the extent at which the quality of this groundwater system has been affected.

- Remediation program that would help to reduce the concentrations of Manganese, Lead and Cadmium should be carried out on Azare groundwater system.
- Periodic monitoring of Azare groundwater system should be initiated as this would help in assessing any changes in the groundwater system.
- Detailed investigation into the distribution of the various forms of individual soluble metal in Azare groundwater system should be carried out.
- Detailed study of the factors that influence the sorption and desorption of metals on suspended and bottom sediments in groundwater system should be carried out with a view to developing a mathematical model for these processes.

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APPENDIX I

Metal Contaminants and their Maximum Contaminant Levels (MCLs) in Drinking Water

METALS	MCL (mg/L)
Potassium	Not Yet Determined
Calcium	Not Yet Determined
Magnesium	Not Yet Determined
Copper	1.3
Zinc	5.0
Manganese	0.05
Lead	0.015
Cadmium	0.005

APPENDIX II

Geographical Map of Bauchi State Showing the Location of Azare

APPENDIX III

Description of the Sampling Sites (Boreholes)

Sampling Site	Description
BH_1	Borehole beside school of science, C.O.E, Azare.
BH_2	Borehole at the back of school of languages, C.O.E, Azare.
BH_3	Borehole in front of Markazul Islam, Jama'are road.
BH_4	Borehole at cooperative, Jama'are road.
BH_5	Borehole at Kazuan Kaji.
BH_6	Borehole at Tashar dan Asabe, Old Kano road.
BH_7	Borehole at Bapah Shanu.
BH_8	Borehole at Dabah Makao.
BH_9	Borehole at Ishawa road, Matsango.
BH_{10}	Borehole at Pillow Qtrs, Matsango.
BH_{11}	Borehole beside Adalchi bakery, Matsango.
BH_{12}	Borehole at Matsango IV
BH_{13}	Borehole at Lailigo
BH_{14}	Borehole at Line Maikaolazan
BH_{15}	Borehole at Sabon Fagi
BH_{16}	Borehole beside Mallam Yakubu resident, Matsango
BH_{17}	Borehole at Odogi I
BH_{18}	Borehole beside Mallam Ibrahim residence, Matsango.
BH_{19}	Borehole at Odogi II
BH_{20}	Borehole at Line Al-amin, Misau road

APPENDIX IV

Description of the Sampling Sites (Hand-Dug Wells)

Sampling Site	Description
W_1	Well at Garin Arab
W_2	Well at Ungua Kwah-Kaban
W_3	Well at Badala (Rijiyar Makam)
W_4	Well at Bakin Line
W_5	Well at Makarahuta
W_6	Well beside Mallam Ayuba's mosque, Makarahuta
W_7	Well opposite Mallam Kundu's residence, Makarahuta
W_8	Well at Sabon pagi
W_9	Well beside Mallam Ibrahim Yaro-Yaro's residence, Royal Hotel street
W_{10}	Well at Tsakuwa Junction
W_{11}	Well beside Azare Bakery Company (ABC) Sardauna road
W_{12}	Rijiya Mangoro, Sardauna road
W_{13}	Well beside Mallam Gambo's residence, Lailiko street
W_{14}	Well opposite Isawa Shopping Complex, Matsango
W_{15}	Well opposite Sheik Ibrahim Arabic Institution, Matsango
W_{16}	Well in front of Jomos Printing Press, Alkali Musa road
W_{17}	Rijiya Alhaji Shiri behind State Library
W_{18}	Well at Sarkin Azare's house, Usman street
W_{19}	Rijiya Alhaji Dan Shehu, opposite Izala mosque, Kazuwan Kaji
W_{20}	Rijiya Alhaji Baba Yo Mai goro, Kazuwan Kaji

APPENDIX V

Range of Concentrations of Potassium Standard Solutions

Standard Solution	Concentration (mg/L)
I	2.00
II	4.00
III	6.00
IV	8.00
V	10.00

APPENDIX VI

Range of Concentrations of Calcium Standard Solutions

Standard Solution	Concentration (mg/L)
I	2.00
II	4.00
III	6.00
IV	8.00
V	10.00

APPENDIX VII

Range of Concentrations of Magnesium Standard Solutions

Standard Solution	Concentration (mg/L)
I	1.00
II	2.00
III	3.00
IV	4.00
V	5.00

APPENDIX VIII

Range of Concentrations of Copper Standard Solutions

Standard Solution	Concentration (mg/L)
I	1.00
II	2.00
III	3.00
IV	4.00
V	5.00

APPENDIX IX

Range of Concentrations of Zinc Standard Solutions

Standard Solution	Concentration (mg/L)
I	1.00
II	2.00
III	3.00
IV	4.00
V	5.00

APPENDIX X

Range of Concentrations of Manganese Standard Solutions

Standard Solution	Concentration (mg/L)
I	2.00
II	4.00
III	6.00
IV	8.00
V	10.00

APPENDIX XI

Range of Concentrations of Lead Standard Solutions

Standard Solution	Concentration (mg/L)
I	1.00
II	2.00
III	3.00
IV	4.00
V	5.00

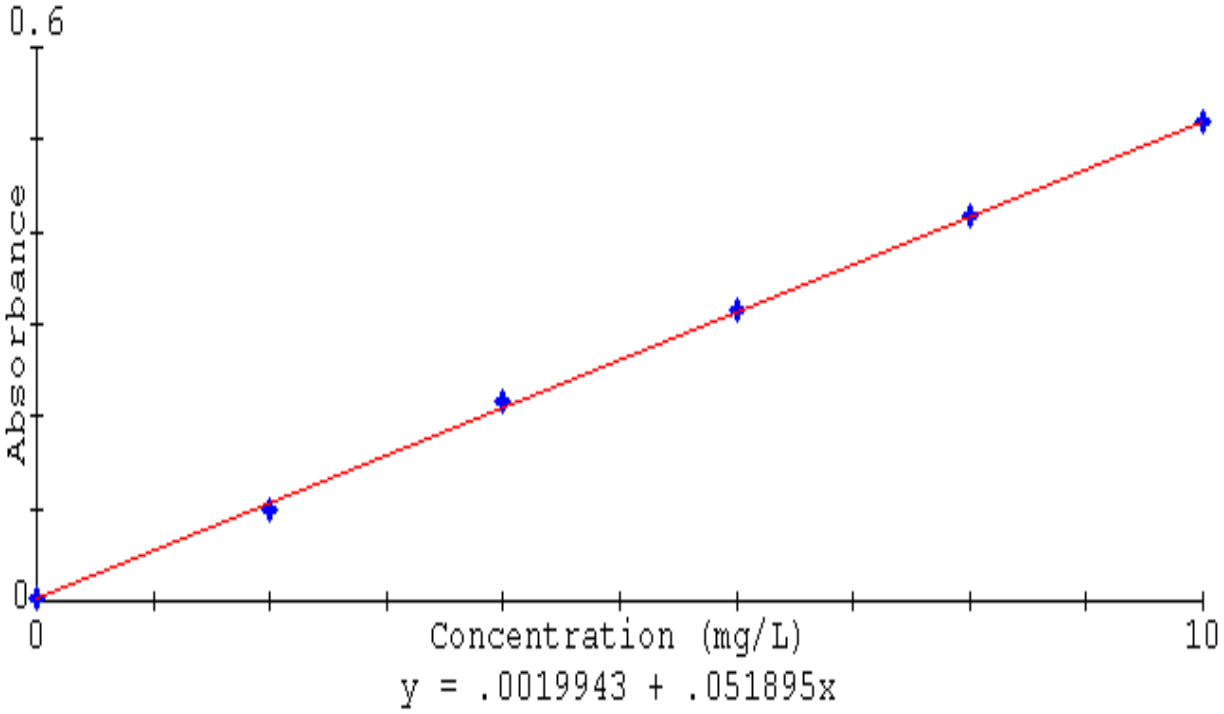
APPENDIX XII

Range of Concentrations of Cadmium Standard Solutions

Standard Solution	Concentration (mg/L)
I	0.01
II	0.02
III	0.03
IV	0.04
V	0.05

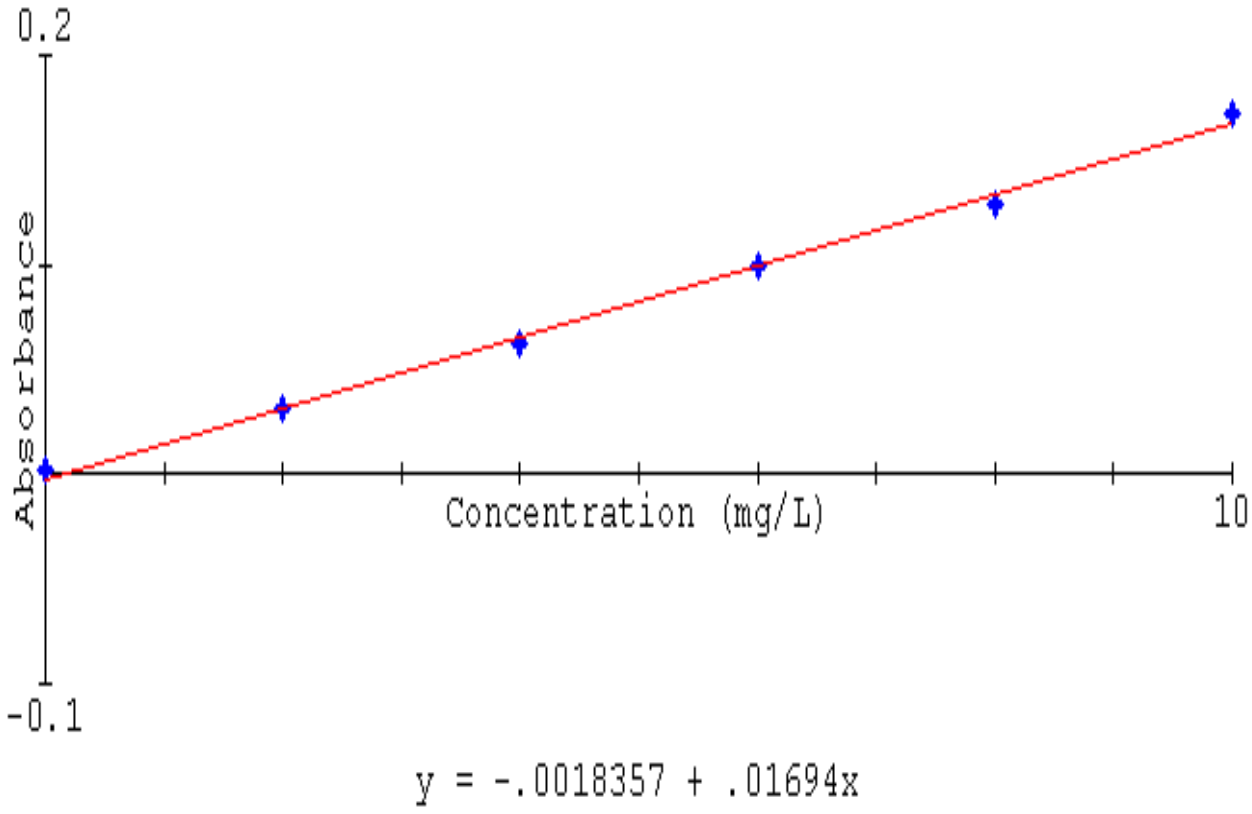
APPENDIX XIII

Calibration Curve for Potassium



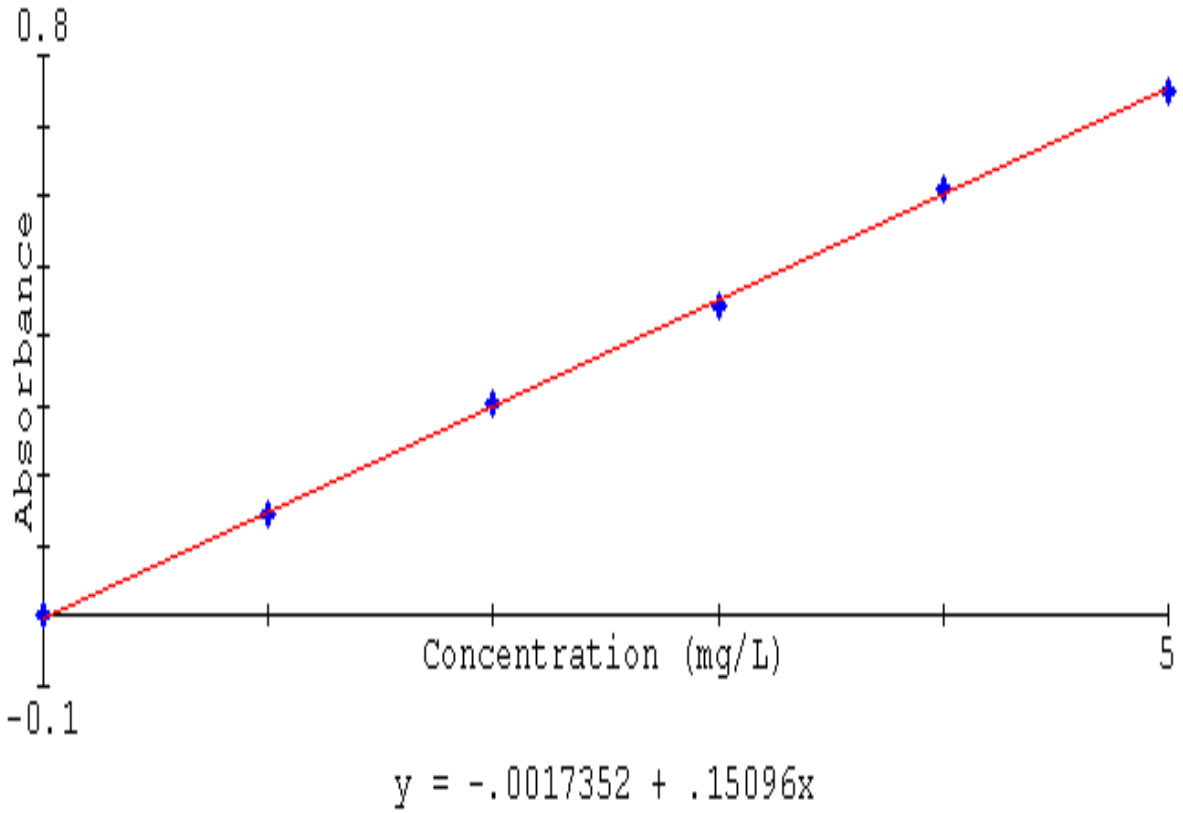
APPENDIX XIV

Calibration Curve for Calcium



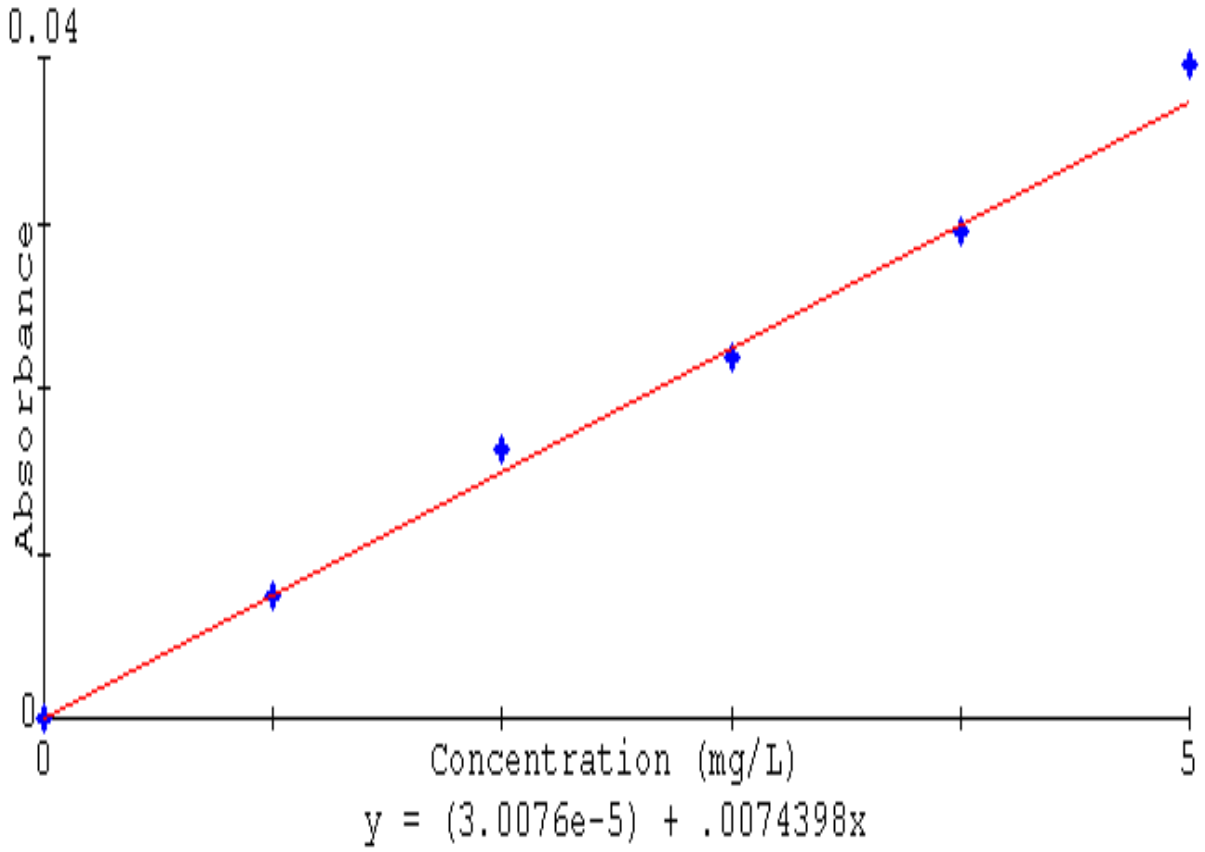
APPENDIX XV

Calibration Curve for Magnesium



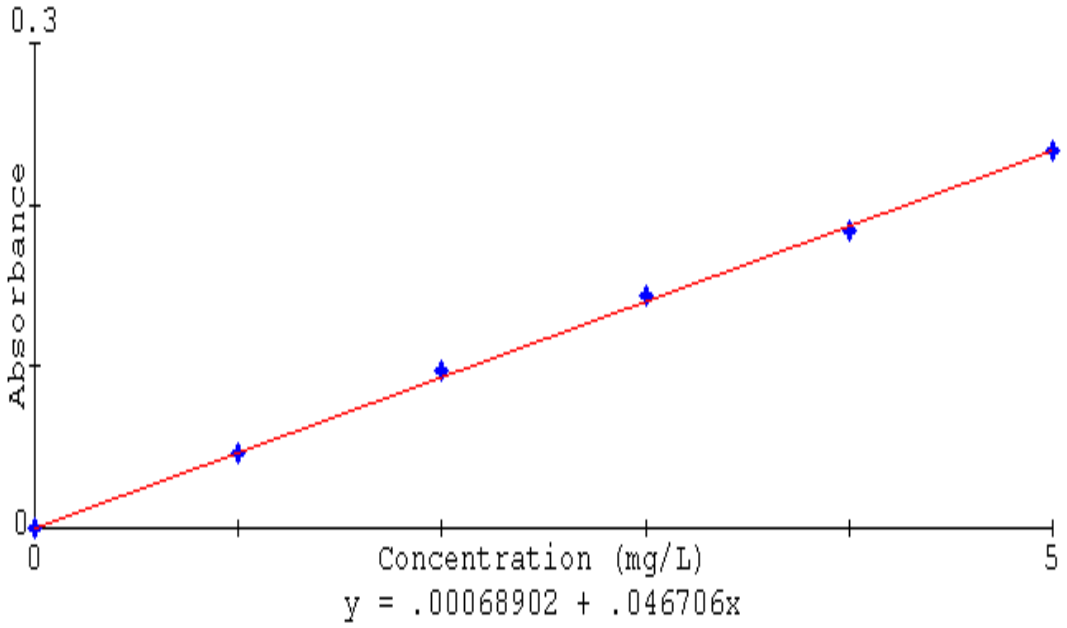
APPENDIX XVI

Calibration Curve for Copper



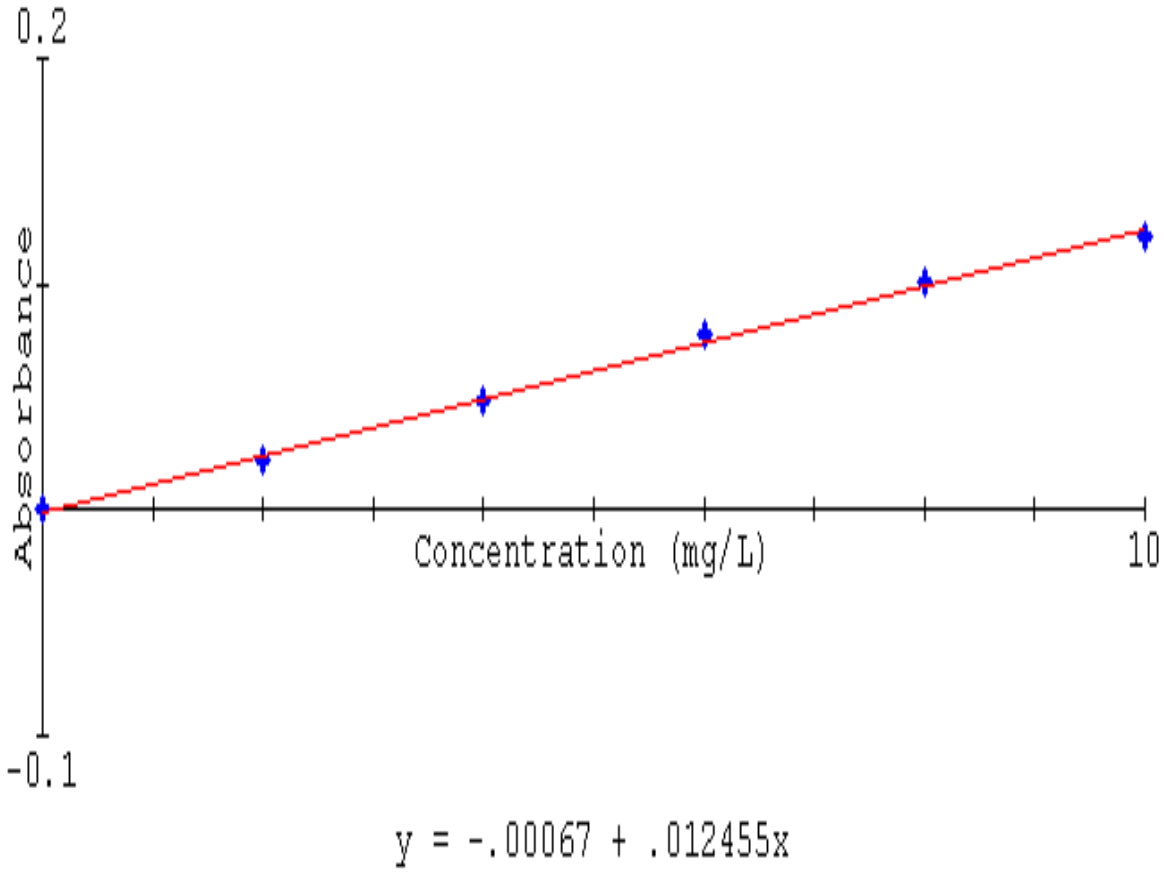
APPENDIX XVII

Calibration Curve for Zinc



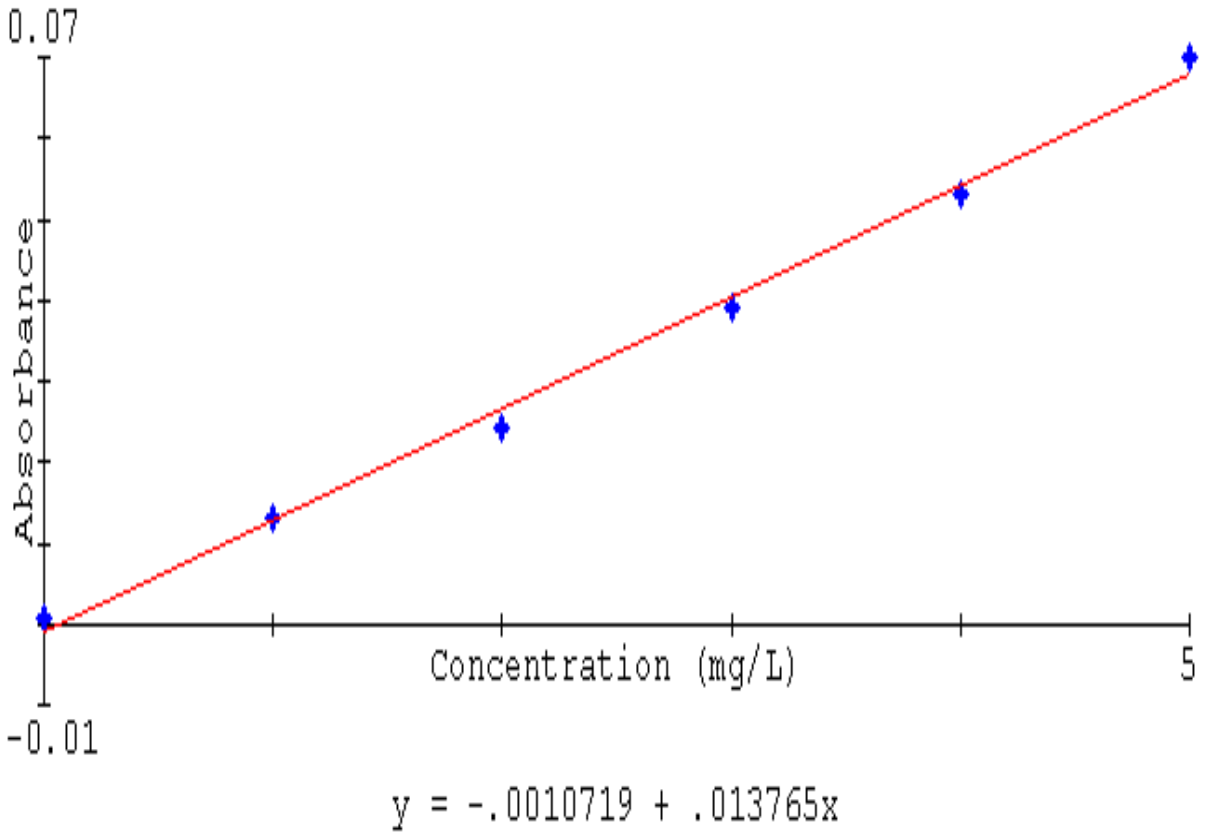
APPENDIX XVIII

Calibration Curve for Manganese



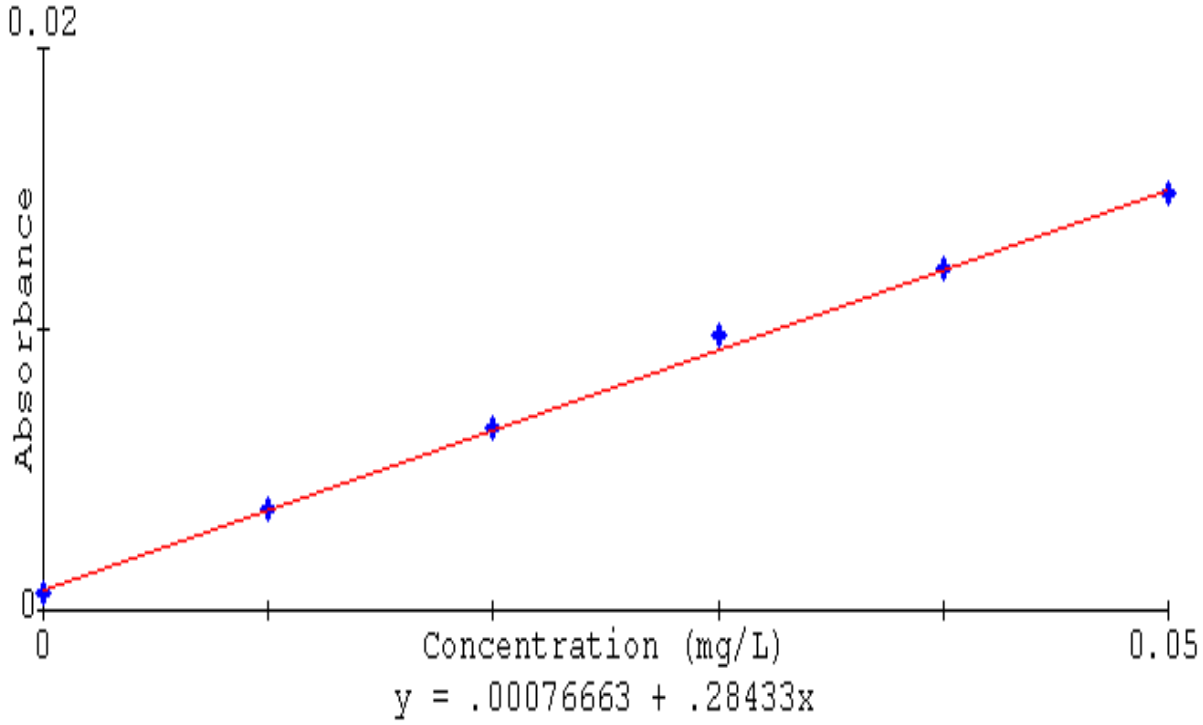
APPENDIX XIX

Calibration Curve for Lead



APPENDIX XX

Calibration Curve for Cadmium



APPENDIX XXI

Formula for Computing F-test

$$F = \frac{S_1^2}{S_2^2}$$

Where

S_1^2 is the larger of the two variances

S_2^2 is the smaller of the two variances

n_1-1 is the degree of freedom for the numerator

n_2-1 is the degree of freedom for the denominator

APPENDIX XXII

Formula for computing t-test Statistics for Independent Samples When the Variances are assumed to be Unequal

$$t = \frac{(\overline{X}_1 - \overline{X}_2) - (\overline{\mu}_1 - \overline{\mu}_2)}{\sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}}}$$

Where :

$\overline{X}_1 - \overline{X}_2$ is the observed difference between the sample means

$\overline{\mu}_1 - \overline{\mu}_2$ is the expected value which is equal to zero when no difference between population means is hypothesized.

n_1 and n_2 are the sample sizes

S_1 and S_2 are the standard deviations of the samples

APPENDIX XXIII

Formula for computing t-test Statistics for Independent Samples When the Variances are assumed to be Equal

$$t = \frac{(\bar{X}_1 - \bar{X}_2) - (\bar{\mu}_1 - \bar{\mu}_2)}{\sqrt{\frac{(n_1-1)S_1^2 + (n_2-1)S_2^2}{n_1 + n_2 - 2}} \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

Where :

$\bar{X}_1 - \bar{X}_2$ is the observed difference between the sample means

$\bar{\mu}_1 - \bar{\mu}_2$ is the expected value which is equal to zero when no difference between population means is hypothesized.

n_1 and n_2 are the sample sizes

S_1 and S_2 are the standard deviations of the samples

APPENDIX XXIV

Concentrations of Total Metal Contaminants in Boreholes (Values Expressed in mg/L)

Sampling Site	Sample	K	Ca	Mg	Cu	Zn	Mn	Pb	Cd
BH_1	A_1	1.0824	0.9025	0.6709	0.6431	0.5366	0.4310	0.1404	ND
BH_2	A_2	0.7094	0.6652	0.3881	0.1411	1.4894	0.2828	0.7337	0.0003
BH_3	A_3	0.5266	0.7888	0.5678	0.0947	0.3042	0.0534	0.1011	0.0031
BH_4	A_4	0.4578	0.8222	0.6201	0.1238	0.1909	0.1111	0.1000	0.0005
BH_5	A_5	0.5890	0.6253	0.4084	0.1342	0.2365	0.1945	0.0644	0.0047
BH_6	A_6	0.3756	0.6221	0.3988	0.2246	0.8034	0.2458	0.0576	0.0089
BH_7	A_7	0.1626	0.3583	0.1347	0.3355	0.1433	0.3345	0.0749	0.0090
BH_8	A_8	0.2075	0.6019	0.3546	0.1500	0.0960	0.4097	0.0488	0.0035
BH_9	A_9	0.1813	0.4089	0.1816	0.1312	0.1573	0.1561	0.0797	0.0082
BH_{10}	A_{10}	0.1567	0.3939	0.1307	0.1722	0.2751	0.2015	0.1300	0.0098
BH_{11}	A_{11}	0.1885	0.4613	0.2099	0.2990	0.3328	0.2328	0.0899	ND
BH_{12}	A_{12}	0.1706	0.4086	0.1873	0.3026	0.1554	0.0710	0.0500	0.0017
BH_{13}	A_{13}	0.3487	0.7877	0.4749	0.1662	0.4169	0.1966	0.0775	0.0042
BH_{14}	A_{14}	0.2367	0.4335	0.2914	0.1896	0.2425	0.1403	0.0691	0.0059
BH_{15}	A_{15}	0.3136	0.5006	0.3005	0.2563	0.1814	0.1100	0.0846	0.0072
BH_{16}	A_{16}	0.1244	0.3382	0.1838	0.3119	0.2091	0.0816	0.1155	0.0039
BH_{17}	A_{17}	0.1549	0.3350	0.1742	0.2928	0.1415	0.1761	0.0438	0.0058
BH_{18}	A_{18}	0.1721	0.5024	0.2667	0.3623	0.1816	0.0986	0.0792	0.0097
BH_{19}	A_{19}	0.1253	0.3660	0.1605	0.3942	0.1954	0.1348	0.1599	0.0110
BH_{20}	A_{20}	0.1816	0.5432	0.2504	0.0461	0.2310	0.0950	0.1682	ND

APPENDIX XXV

Concentrations of Total Metal Contaminants in Hand-Dug Wells

(Values Expressed in mg/L)

Sampling Site	Sample	K	Ca	Mg	Cu	Zn	Mn	Pb	Cd
W_1	A_{21}	0.3689	0.3917	0.1704	0.1068	0.2368	0.1364	0.1966	0.0066
W_2	A_{22}	0.6891	0.6347	0.4401	0.1072	0.3051	0.1310	0.1444	0.0091
W_3	A_{23}	0.3082	2.3922	2.7034	0.3286	0.3068	0.1884	0.1398	0.0105
W_4	A_{24}	0.6187	2.8432	2.5649	0.4390	0.2916	0.1100	0.1814	ND
W_5	A_{25}	2.0145	1.5921	1.6443	0.1381	0.1417	0.2601	0.0573	0.0007
W_6	A_{26}	2.7262	5.1730	4.0780	0.0713	0.1053	0.6313	0.0764	0.0023
W_7	A_{27}	1.1297	0.7942	0.8081	ND	0.1272	0.1918	0.0462	0.0037
W_8	A_{28}	1.0610	1.0709	0.8343	ND	0.3083	0.0999	0.0393	0.0045
W_9	A_{29}	0.8866	0.6282	0.4432	0.0367	0.1130	0.0442	0.1295	0.0074
W_{10}	A_{30}	0.5659	0.9084	0.3941	0.0107	0.3217	0.2003	0.0917	0.0024
W_{11}	A_{31}	0.3285	0.5719	0.3383	0.0096	0.1309	0.1707	0.0564	0.0074
W_{12}	A_{32}	0.3951	0.6260	0.3565	ND	0.1695	0.1169	0.0769	ND
W_{13}	A_{33}	0.3553	0.8276	0.4250	0.0828	0.1858	0.1438	0.0747	0.0009
W_{14}	A_{34}	2.1647	1.2726	0.8332	0.0832	0.1666	0.0563	0.0706	0.0025
W_{15}	A_{35}	0.3692	0.4567	0.3324	0.0746	0.1484	0.0741	0.0393	0.0044
W_{16}	A_{36}	0.3219	0.4647	0.3532	0.1013	0.1414	0.0790	0.1289	0.0080
W_{17}	A_{37}	0.5408	0.9200	0.7360	0.0688	0.0535	0.0698	0.1120	0.0088
W_{18}	A_{38}	1.1485	0.7753	0.5021	0.1012	0.1600	0.1542	0.1490	ND
W_{19}	A_{39}	0.6861	0.8689	0.5511	0.0744	0.1656	0.1098	0.0245	0.0011
W_{20}	A_{40}	0.9013	0.9031	0.5779	0.0722	0.2008	0.2220	0.0957	0.0024

APPENDIX XXVI

Concentrations of Soluble Metal Contaminants in Boreholes (Values Expressed in mg/L)

Sampling Site	Sample	K	Ca	Mg	Cu	Zn	Mn	Pb	Cd
BH_1	B_1	0.7958	0.5672	0.5645	0.0816	0.3232	0.3211	0.0593	0.0042
BH_2	B_2	0.6178	0.4607	0.2978	0.0485	0.4763	0.1593	0.0165	0.0057
BH_3	B_3	0.5067	0.7224	0.5424	0.0284	0.1506	0.0218	ND	0.0009
BH_4	B_4	0.3749	0.7263	0.5969	0.0587	0.1566	0.0887	0.0694	0.0004
BH_5	B_5	0.5806	0.4559	0.4059	0.0562	0.2348	0.0633	ND	0.0017
BH_6	B_6	0.3342	0.5348	0.3753	0.0228	0.3733	0.1187	0.0273	ND
BH_7	B_7	0.1244	0.3399	0.1275	0.0804	0.1454	0.1796	0.0563	ND
BH_8	B_8	0.1699	0.4704	0.3320	0.0230	0.0552	0.1254	0.0167	ND
BH_9	B_9	0.1666	0.3418	0.1466	0.0227	0.1559	0.1116	0.0273	0.0005
BH_{10}	B_{10}	0.1190	0.2560	0.1244	0.0342	0.2350	0.1589	ND	0.0028
BH_{11}	B_{11}	0.1651	0.2959	0.1824	0.0074	0.1756	0.1309	0.0749	ND
BH_{12}	B_{12}	0.1643	0.3189	0.1717	0.0689	0.1271	0.1000	0.0622	0.0003
BH_{13}	B_{13}	0.2596	0.6562	0.4558	0.0747	0.0942	0.1157	0.0223	0.0010
BH_{14}	B_{14}	0.2335	0.4240	0.2063	0.0378	0.1360	0.1285	0.0273	0.0022
BH_{15}	B_{15}	0.3097	0.4400	0.2945	0.0936	0.1090	0.0439	0.0114	ND
BH_{16}	B_{16}	0.1150	0.3166	0.0933	0.0237	0.1604	0.0486	0.0574	0.0050
BH_{17}	B_{17}	0.1405	0.3032	0.1545	0.0917	0.1145	0.0791	0.0330	0.0012
BH_{18}	B_{18}	0.1036	0.4230	0.2463	0.0327	0.1503	0.0887	0.0609	0.0001
BH_{19}	B_{19}	0.0951	0.2467	0.1426	0.0624	0.1123	0.0741	0.0635	ND
BH_{20}	B_{20}	0.1288	0.3877	0.2448	ND	0.2190	0.0160	0.0773	0.0001

APPENDIX XXVII

Concentrations of Soluble Metal Contaminants in Hand-Dug Wells

(Values Expressed in mg/L)

Sampling Site	Sample	K	Ca	Mg	Cu	Zn	Mn	Pb	Cd
W_1	B_{21}	0.3577	0.2823	0.1609	0.0085	0.1547	0.0437	0.0573	0.0018
W_2	B_{22}	0.5593	0.4673	0.3878	0.0291	0.1376	0.1090	ND	0.0034
W_3	B_{23}	0.2230	2.1683	2.4556	0.1243	0.1551	0.1566	0.0885	0.0054
W_4	B_{24}	0.5670	2.3528	2.3766	0.1044	0.2373	0.1041	0.0699	0.0060
W_5	B_{25}	2.0014	1.5901	1.6210	0.0427	0.1156	0.2665	0.0082	0.0005
W_6	B_{26}	2.5669	5.0761	3.1465	0.0104	0.2403	0.5859	0.0476	0.0003
W_7	B_{27}	1.0678	0.7110	0.7887	ND	0.1564	0.1443	0.0372	0.0020
W_8	B_{28}	1.0588	1.0542	0.8227	0.0056	0.1381	0.0778	0.0139	0.0036
W_9	B_{29}	0.8711	0.6012	0.4407	0.0059	0.1307	0.1919	0.0637	0.0056
W_{10}	B_{30}	0.5446	0.7640	0.3832	0.1076	0.1084	0.2068	0.0799	0.0009
W_{11}	B_{31}	0.3241	0.5700	0.2676	0.0466	0.1043	0.1284	0.0262	0.0078
W_{12}	B_{32}	0.3081	0.6213	0.3002	ND	0.1627	0.1144	0.0246	ND
W_{13}	B_{33}	0.3447	0.6817	0.3818	0.0297	0.1321	0.1237	0.0359	0.0004
W_{14}	B_{34}	2.1466	1.1370	0.8041	0.0393	0.1169	0.0134	0.0576	ND
W_{15}	B_{35}	0.3522	0.4238	0.3241	0.0101	0.1209	0.0560	0.0156	0.0001
W_{16}	B_{36}	0.2993	0.4376	0.3502	0.0375	0.1102	0.0992	0.0657	0.0020
W_{17}	B_{37}	0.5025	0.6089	0.7173	0.0126	0.0538	0.0700	0.0458	0.0032
W_{18}	B_{38}	1.1089	0.7200	0.4380	0.0290	0.1598	0.1293	ND	ND
W_{19}	B_{39}	0.6764	0.6018	0.4516	0.0189	0.1200	0.1051	0.0074	0.0009
W_{20}	B_{40}	0.8022	0.7371	0.5079	0.0129	0.1596	0.2037	0.0574	0.0061